LESSON 12

A-PDF Merger DEMO : Purchas

GENERAL ORGANIC CHEMISTRY

Organic chemistry, seemingly a vast area of chemistry, can be made concise, if the fundamentals are studied through simple and systematic approach. Entire organic chemistry can be controlled and conceived if this lesson is mastered well. Here, we have taken all the concepts starting from basics like bond cleavage, types of reagents, various effects operating in compounds and their roles, giving proper emphasis on IIT-JEE syllabus.

The concepts studied in this lesson would be a useful tool in our hands, which enable us to foretell the mechanism or product of a given reaction.

IIT-JEE Syllabus: *Hybridization of carbon; Sigma and pi-bonds; Shapes of molecules; IUPAC nomenclature of simple organic compounds (only hydrocarbons, monofunctional and bifunctional compounds); Inductive and resonance effects on acidity and basicity of organic acids and bases; Hyperconjugation; Reactive intermediates produced during homolytic and heterolytic bond cleavage; Formation, Structure and Stability of carbocations and free radicals.*

At the outset of the discussion on organic chemistry, we must make it clear that the fundamentals (involving bond cleavage, various intermediates and their reactivities, types of reagents, field effects etc.) are the backbone of entire organic chemistry. These concepts will be useful in understanding the organic chemistry as a whole.

1. TYPES OF BOND CLEAVAGE

A covalent bond between two atoms can be broken in two ways–

(a) Homolytic cleavage: $R\text{–}X \longrightarrow \dot{R} + \dot{X}$

(b) Heterolytic cleavage $R\text{–}X \longrightarrow R^{\oplus} + X^{\ominus}$ or $R^{\oplus} + X^{\ominus}$

In the first cleavage, each atom separates with one electron leading to the formation of highly reactive intermediates called free radicals. In the second type of fission, one atom may hold on both the electrons leaving none for the other, resulting in a negative and a positive ion (or ion pair). Homolytic cleavage occurs generally in the gas phase or in solution in non-polar solvents and is catalysed by ultraviolet light or high temperature or by radical initiators like peroxides. Heterolytic cleavage occurs in polar solvents because of the ease of separation of charge and stabilization of the resultant ion-pairs through solvation. In such heterolytic fission, the charged species formed are either carbon bearing positive charge called carbocation or carbon bearing negative charge called carbanion.

2. TYPES OF REAGENTS

There are basically two types of reagents used in organic chemistry, the electrophiles and nucleophiles. In organic chemistry, the interaction of electrophile i.e. electron pair acceptors and nucleophiles i.e. electron pair donors is generally observed. Electrophiles in other words are called Lewis acids & nucleophiles are called Lewis bases.

Electrophiles (Lewis acid)

Soft Acids	Hard Acids
(Hg_2^{2+}, Fe^{2+}, Ag^{+} etc.) Metals of lower oxidation state	(Fe^{3+}, $H^{\oplus}$, Li^{+}, Na^{+} etc.) Metals of relatively higher oxidation state

Nucleophiles (Lewis bases)

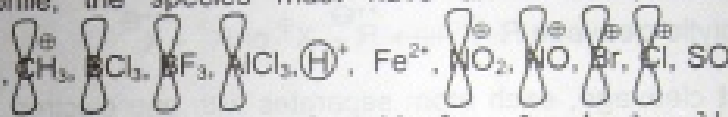
Soft bases	Hard bases

By HSAB theory, soft acid binds soft base well and hard acid binds hard base well. Soft acids are those species, which are easily *oxidisable, possess polarisable electron cloud, low electronegativity*. For example, Fe^{2+}, Hg_2^{2+}, $C^{\oplus\oplus}$ and Ag^{+}.

Hard acids are those which are *difficult to oxidise, have higher electronegativity, high polarizing power*. For example, Fe^{3+}, C^+ and H^+.

There is no hard & fast rule to differentiate those species. Similarly, hard bases possess N, O or F donor atoms, which are *difficult to oxidise, difficult to polarize and have high electronegativity*. Hard bases prefer to act as bases. For example, $:\ddot{O}H^{\ominus}$, $:NH_2^{\ominus}$, $\ddot{O}CH_3^{\ominus}$, $\ddot{F}^{\ominus}$, etc.Soft bases have electron pair donor atoms, *which are easy to oxidise, easy to polarize and have lower electronegativity*. For example, $:\ddot{S}H^{\ominus}$, $HSO_3^{\ominus}$, etc. Soft bases are good nucleophiles. HSAB principle, which stems from thermodynamic interaction also applies in reactions in organic chemistry.

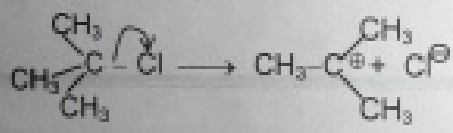
To be an electrophile, the species must have an element, which has suitable vacant orbital. For example, $\overset{\oplus}{C}H_3$, BCl_3, BF_3, $AlCl_3$, $\overset{\oplus}{(H)}$, Fe^{2+}, $NO_2^{\oplus}$, $\overset{\oplus}{N}O$, $\overset{\oplus}{Br}$, $\overset{\oplus}{Cl}$, SO_3, etc. Similarly,

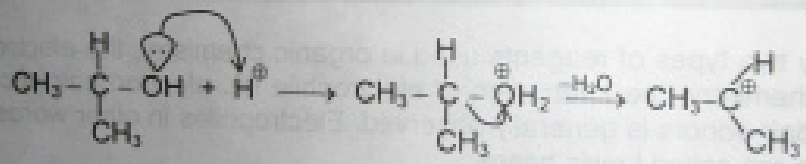


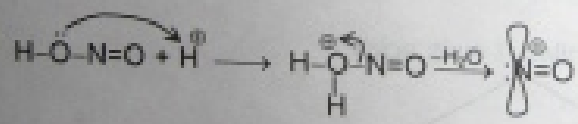
the nucleophiles should have at least one atom with lone pair of electrons for donations.

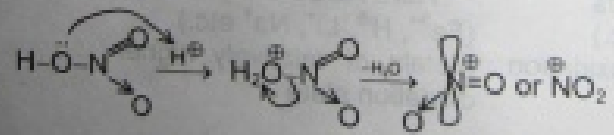
For example, F^-, Br^-, Cl^-, OH^-, NH_3, H_2O, CH_3^-, NH_2^-, CN^-, NC^-, etc.

The generation of electrophiles can take place in various ways but all originate from heterolytic bond cleavage. For example,

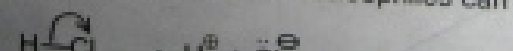
(i) 

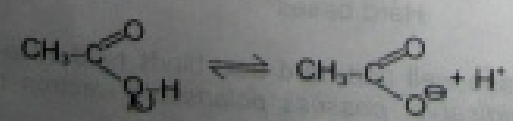
(ii) 

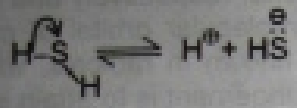
(iii) 

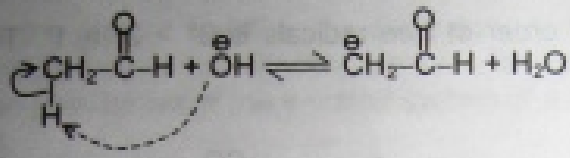
(iv) 

Similarly, the generation of nucleophiles can also take place by heterolytic cleavage.









3. VARIOUS INTERMEDIATES

Whenever a reaction takes place in organic chemistry, the reactants are not directly transformed into the products. The reaction proceeds via some intermediates, which are formed during the course of reaction and are not very stable species. The most common transient intermediates formed are radicals, carbocations and carbanions but other reactive intermediates possible are carbenes, nitrenes and benzynes. The formation of these intermediates and their characteristic reactions have been dealt here in brief.

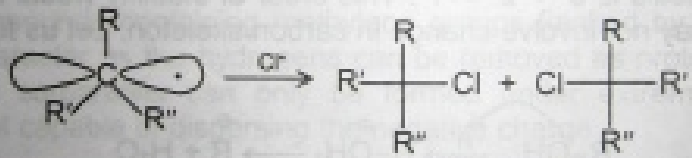
3.1 FREE RADICALS

Their formation is initiated mostly by ultraviolet light. For example,

$$Cl{-}Cl \xrightarrow{h\nu} 2\dot{C}l$$

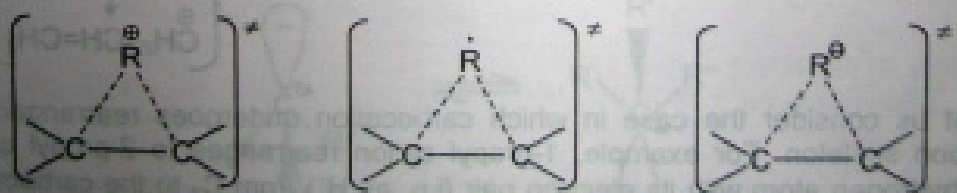
$$R{-}H + \dot{C}l \longrightarrow \dot{R} + H{-}Cl$$

This alkyl group bearing an odd unpaired electron is called alkyl radical. The radicals are electron deficient and paramagnetic in nature. A free radical has carbon in the sp^2 hybridised state, thus exhibit planar (flat) structure. If a free radical with three different atoms or group of atoms is attacked by another radical, it leads to the generation of a stereocentre, existing as enantiomeric pair.



Enantiomeric pair

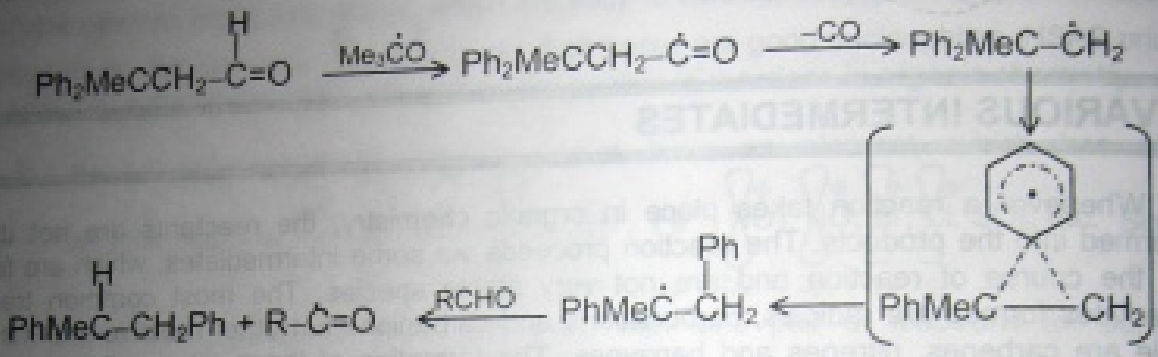
The free radicals can act as electrophiles, which attack at the site of high electron density on the substrate. Free radicals have very less or no tendency to rearrange to give a more stable radical.



Carbocation T.S. Radical T.S. Carbanion T.S.

Whenever a intermediate rearranges, it goes through a transition state. The transition states for the rearrangement of carbocation, radical and carbanion are shown above.

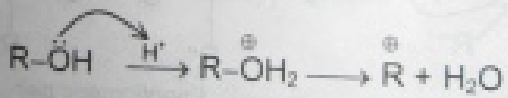
These transition states involve two, three and four electrons, respectively and electrons in excess of two can be accommodated only in an antibonding molecular orbital of much higher energy. However as with carbanions, 1, 2-aryl shifts are also known in radicals, which involve stabilized, bridged transition state. The driving force for the rearrangement is to attain stability. At this state, hold this fact that the stability order of free radicals is 3° > 2° > 1°. This order of stability would be explained later. For example,

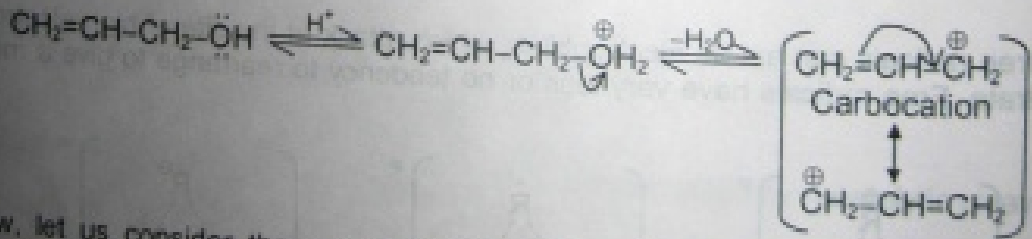


The rearranged radical is more stable than the original one not only because the former is primary and the latter is tertiary but also because it is stabilized by delocalization of the unpaired electron over the π-orbital system of benzene nucleus. It is significant that only Ph migrates, despite the fact that migration of Me would yield even more stabilized radical, $Ph_2\dot{C}CH_2Me$. This probably reflects the energetic advantage of the migration of Ph via a bridged delocalized transition state. When no Ph group is present, as in $EtMe_2CCH_2CHO$, no migration takes place at all and the end product is $EtMe_2CCH_3$.

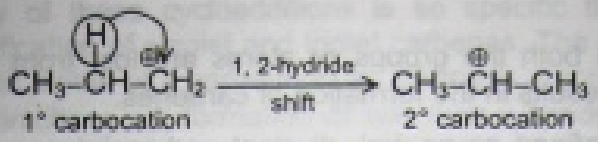
3.2 CARBOCATIONS

Carbocation is the carbon containing intermediate bearing a positive charge and having a sextet of electrons in its outermost shell. The carbocation can act as a electrophile. The most characteristic feature of carbocations is that they undergo rearrangements readily (if possible). The driving force for the rearrangement is to attain stability. At this stage, digest this fact that the stability order of free radicals is 3° > 2° > 1°. This order of stability would be explained later. The rearrangement may or may not involve change in carbon skeleton. Let us first see the carbocation formation from alcohols.

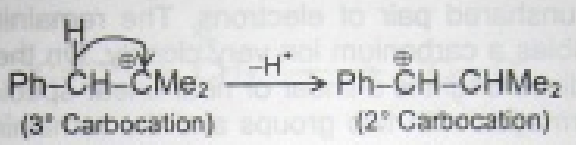




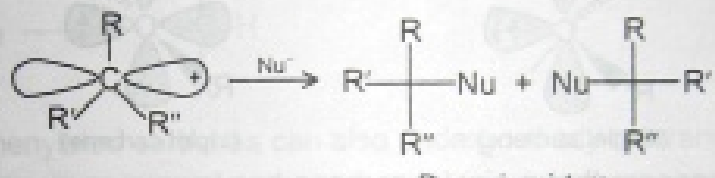
Now, let us consider the case in which carbocation undergoes rearrangement without change in carbon skeleton. For example, 1-propyl cation rearranges to 2-propyl cation by the migration of a hydrogen atom with its electron pair (i.e. as H^-) from C_2 to the carbocationic C_1 by 1, 2-hydride shift.



This reflects the greater stability of a secondary carbocation rather than a primary carbocation. However, shift in the reverse direction can also take place where this makes available the greater delocalization possibilities of the π-orbital system of a benzene ring. (i.e. Tertiary ⟶ Secondary). For example,

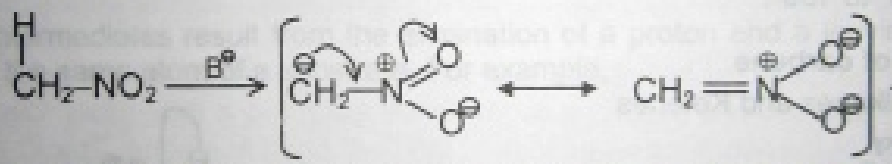


Carbocation has a trigonal planar structure, as the carbon atom of carbocation is also sp^2 hybridised. A carbocation can act as an electrophilic reagent and it leads to the formation of racemic mixture.



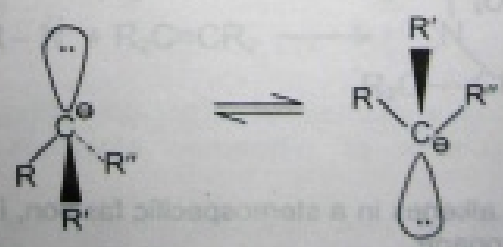
3.3 CARBANIONS

Carbanions are anions of carbon, generated by the removal of one of the groups attached to a carbon atom without removing the bonding electrons. For example, nitromethane reacts with alkali to yield an anion, which is stabilized by resonance.



In general, compounds containing methylene groups flanked by nitro, cyano or carbonyl groups show acidic character as the hydrogens can be removed as protons leaving a resonance stabilized anion. Alkyl carbanions can only be formed under extreme conditions, since the attached groups are not capable of dispersing the negative charge.

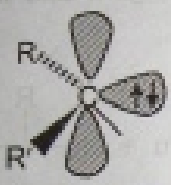
Carbanion assumes a pyramidal configuration, as carbon atom here is sp^3 hybridised. The unshared electron pair would be accommodated in an sp^3 hybridised orbital. The unshared electron pair would be accommodated in an sp^3 orbital. The carbanions readily undergo pyramidal inversion also called umbrella effect.



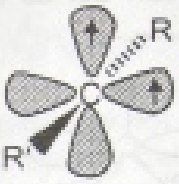
3.4 CARBENE

A reaction in which both the groups or atoms are lost from the same carbon is called α-elimination reaction and results in the formation of carbenes.

Carbenes can be defined as neutral, divalent carbon intermediates in which a carbon is covalently bonded to two atoms and has two non-bonded orbitals containing two electrons between them. Theoretical considerations suggest that there are two possible kinds of carbenes, singlet and triplet. In the singlet state, a carbon atom is presumed to approximate sp^2 hybridization. Two of the three sp^2 hybrid orbitals are utilized in forming two covalent bonds whereas the third hybrid orbital contains the unshared pair of electrons. The remaining p-orbital remains vacant. Thus singlet carbene resembles a carbonium ion very closely. On the other hand, carbon atom of a triplet carbene is sp hybridized and it is a linear or near-linear species. These two hybrid orbitals are involved in the bond formation with two groups and the remaining two electrons are placed, one each, in the equivalent, mutually perpendicular p_y and p_z orbitals. These electrons have parallel spins and a carbene with this structure is said to be in a triplet state.



(singlet carbene)

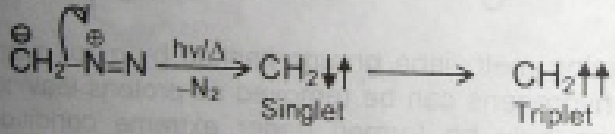


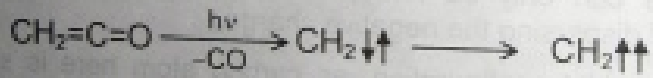
(triplet carbene)

At first sight, it appears that a singlet carbene has lower energy as the unshared electron pair is in a sp^2 hybrid orbital but the consideration of the electron repulsion energy that must be overcome to pair two electrons in a single orbital places it at a higher energy level than a triplet structure. Thus, the triplet state of a carbene is more stable than the singlet state. Electron spin resonance (esr) studies have also confirmed that for aryl and diaryl carbenes the ground state is their triplet structure. These studies have also revealed that triplet carbenes are not linear but have a bond angle of 140° to 150°.

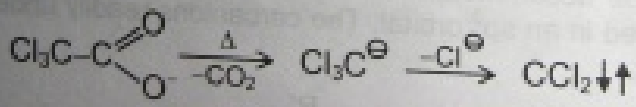
Generation of carbene

(a) From Diazoalkanes and Ketenes





(b) From carbanions



Reactions of carbene

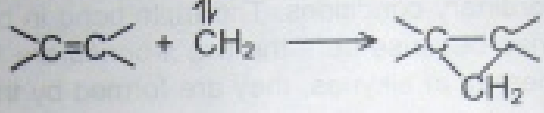
(a) Cycloaddition reactions

(b) Insertion reactions

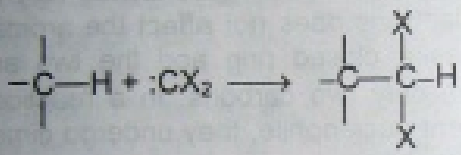
Singlet carbenes add to alkenes in a stereospecific fashion, i.e. the stereochemistry of the alkene is retained in the cyclopropane.

In contrast, the addition of triplet carbenes to alkenes takes place non-stereospecifically.

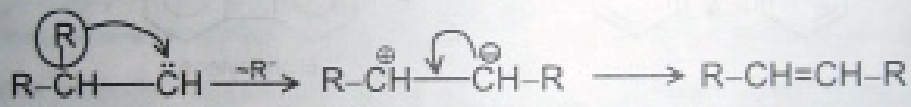
The stereochemistry of these cycloadditions is so specific that it may be used as a diagnostic test for the identification of singlet and triplet carbenes. The difference in the behaviour between these two electronic states of a carbene to an alkene is a concerted process as there is no spin restriction on the simultaneous formation of two new σ-bonds of the cyclopropane and hence it is a stereospecific process. In contrast, the cycloaddition of a triplet carbene is a step-wise process. The first step leads to a triplet diradical, which undergoes spin inversion, before it forms cyclopropane. Since this diradical has a C–C single bond, there is a possibility of free rotation about that bond. If this rotation is faster than spin inversion, the reaction becomes non-stereospecific.



Frequently, carbenes can be inserted into a C–H bond, to increase the length of carbon chain.

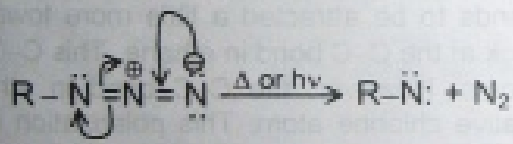


Alkylated and phenylated carbenes can also undergo ready rearrangement, to directly give final product (Alkene).



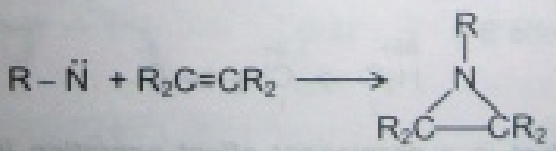
3.5 NITRENE

Such intermediates result from the elimination of a proton and a leaving group (generally halogen) from the same atom of a substrate. For example,



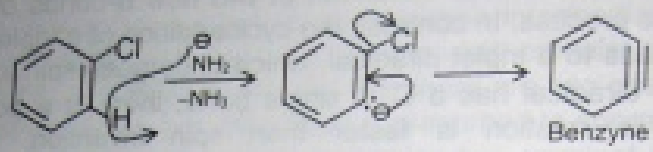
Nitrenes are also electrically neutral nitrogen containing species with two unshared pairs and one bond pair of electrons. Here, nitrogen is the electron deficient atom.

The reactions of nitrenes are similar to those of carbenes. Thus, nitrenes also undergo addition to C=C bonds and insertion into C–H bonds. For example,



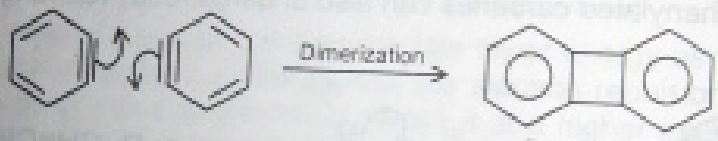
3.6 BENZYNE

These intermediates are generated by the elimination of α-proton and a leaving group (generally halogen) from the adjacent carbons from a benzene ring system. For example,



Benzynes are very reactive. Neither benzyne nor any other aryne (substituted benzyne) has yet been isolated under ordinary conditions. The triple bond in benzynes is not identical with the formal triple bond of alkynes because here the two π-bonds are formed by the overlapping of p_z–p_z and sp^2–sp^2 orbitals whereas in alkynes, they are formed by the overlap of p_z–p_z and p_y–p_y orbitals.

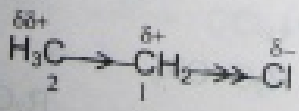
It should be noted that the π-bond (resulted from sp^2–sp^2 overlap) is a very weak bond, which can be easily ruptured by the attack of a nucleophile, thus making benzynes very reactive. Another feature to be noted is that the extra pair of electrons does not affect the aromaticity of benzene nucleus. The original sextet still functions as a closed ring and the two additional electrons are merely located in a π-orbital that covers only two carbons. In a reaction where benzyne is formed, if the solution does not have sufficient nucleophile, they undergo dimerization to give biphenylene. Benzynes are not attacked by electrophiles.



Biphenylene

4. INDUCTIVE EFFECT

In a covalent single bond between unlike atoms, the electron pair forming σ-bond is never shared equally between the two atoms. It tends to be attracted a little more towards the more electronegative atom of the two. First let us look at the C–C bond in ethane. This C–C bond has no polarity because it connects two similar atoms. However, the C–C bond in ethyl chloride is polarized by the presence of the electronegative chlorine atom. This polarization is actually the sum of three effects. In the first of these, the C_1 atom has been deprived of some of its electron density by the higher electronegativity of Cl. Secondly, the electron deficiency of C_1 is partially compensated by drawing the C–C electrons closer to itself, resulting in polarization of this bond and a slight positive charge on the C_2 atom. Thirdly, the polarization of the C–C bond causes a (slight) polarization of three methyl C–H bonds. The effect of C_1 on C_2 is less than the effect of Cl on C_1 atom.



Thus, ***inductive effect is a permanent effect operating in the ground state of the molecule, involving displacement of σ-bonding electrons towards atom of higher electronegativity.***

In addition to such inductive effect operating through the σ-bonds in a compound, an analogous effect can also operate either through the space surrounding the molecule or in solution via the molecules of solvent that surround it, which is called field effect. A point of distinction between the two effects is that the inductive effect depends only the nature of bonds

while the field effect depends on the geometry of the molecule. However, in many cases, it is not possible to distinguish between inductive effect and field effect. But in general, reference to an inductive effect is assumed to include any such field effect.

In ethyl chloride, Cl is said to have an electron withdrawing –I effect. There are other type of groups, which exert electron releasing +I effect. Thus, the substituents or functional groups can be classified as electron-withdrawing (–I) or electron-donating (+I) groups relative to hydrogen.

The order of decreasing inductive effects of most common groups is as follows,

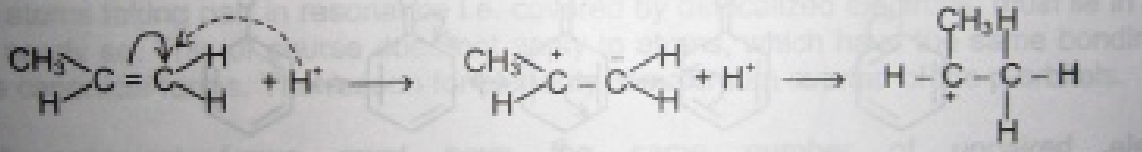
+I groups: $-O^-$, $-CO_2^-$, $-CR_3$, $-CHR_2$, $-CH_2R$, $-D$

–I groups: $-NR_3^+$, $-SR_2^+$, $-NH_3^+$, $-NO_2$, $-SO_2R$, $-CN$, $-CO_2H$, $-F$, $-Cl$, $-Br$, $-I$, $-OAr$, $-COOR$, $-OR$, $-COR$, $-SH$, $-OH$, $-C{\equiv}CR$, $-Ar$, $-CH{=}CR_2$

For measurements of relative inductive effects, hydrogen is chosen as reference in the molecule CR_3–H. If the H-atom in this molecule is replaced by X (an atom or group of atoms), and the electron density in the CR_3 part of the molecule is less than in CR_3–H, then X is said to have a –I effect. If the electron density in the CR_3 part is greater than in CR_3–H, then X is said to have a +I effect. Deuterium is also electron donating with respect to hydrogen. Amongst the sp^3, sp^2 and sp hybridized carbons, the order of –I effect is $sp > sp^2 > sp^3$.

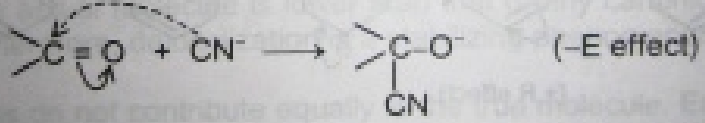
5. ELECTROMERIC EFFECT

This is a temporary effect which involves complete transfer of a shared pair of π-electrons towards one of the atoms linked by a multiple bond at the demand of attacking reagent. The atom receiving the electron pair acquires a unit negative charge, while the other atom becomes positively charged. When the electron transfer takes place towards the attacking reagent, it is called ***+ E effect***.



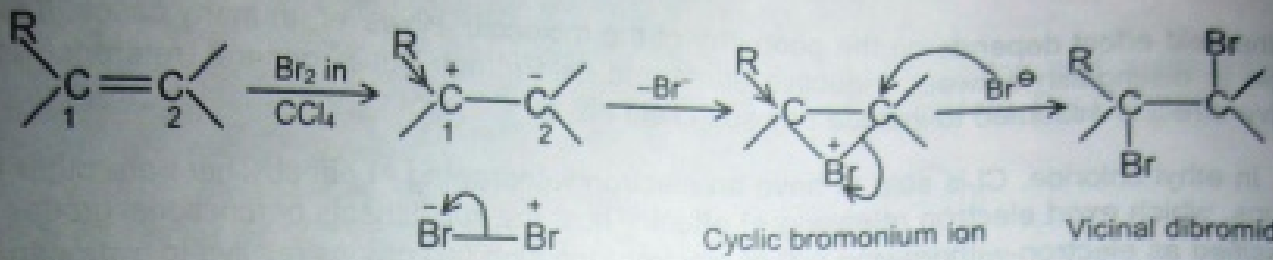
Isopropyl carbonium ion
(+ E effect)

And when the electron transfer takes place away from the attacking reagent, it is called ***– E effect***.



(–E effect)

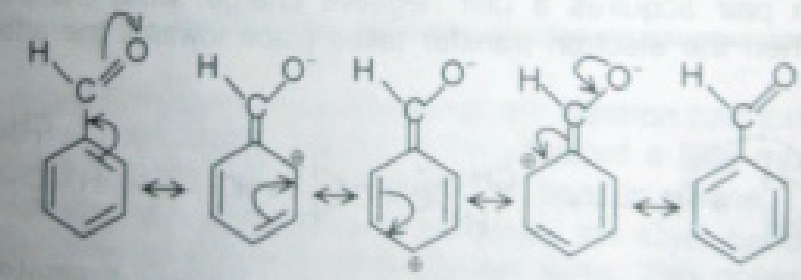
The most common example of the electromeric effect is the reaction of an alkene with bromine in CCl_4.



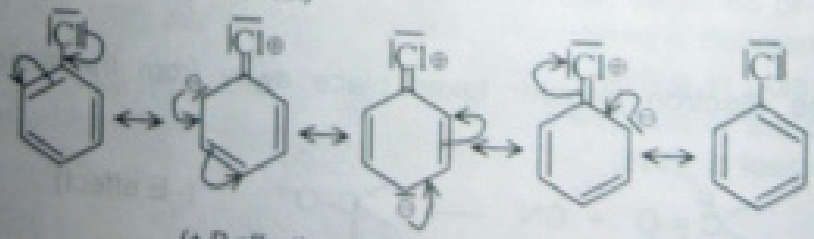
In this reaction, when reagent (bromine) approaches alkene, the temporary polarization develops on the alkene with C_2 atom gaining a negative charge and C_1 atom acquiring positive charge (as it can be compensated by the +I effect of R group). The alkenes being electron rich compounds (due to the presence of π-electron cloud) are attacked by the electrophile (Br^+) to give a cyclic bromonium ion. Here, the formation of cyclic bromonium ion as intermediate is possible because bromine has large size and possess the lone pair, which can be donated to the carbon simultaneously. The cyclic bromonium ion is then attacked by Br^- from the opposite side of the 3-membered cyclic intermediate to give the resultant product.

6. RESONANCE EFFECT

Formation of a centre of high and low electron density by the transfer of π-electrons from one part of conjugated (alternate single and double bonds) π-system to the other is called ***Resonance effect or Mesomeric effect***. This is a permanent effect, which occurs in the ground state of the molecule. Groups, which withdraw electrons from the conjugated system are said to possess –R or –M effect. (e.g. $-NO_2$, –CN, >C=O). The groups, which donate electrons to the conjugated system are said to possess + R or + M effect. (e.g. –X, $-NH_2$, –OH, $-OCH_3$).



(– R effect)



(+ R effect)

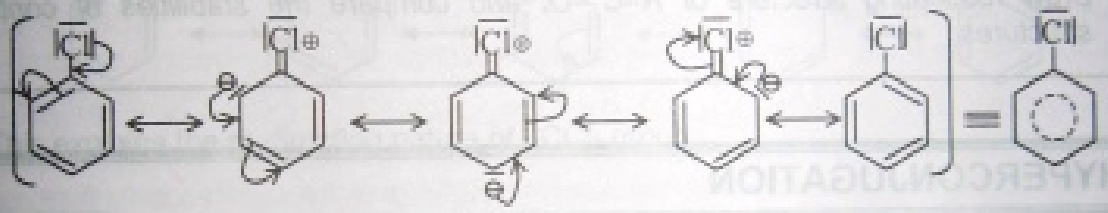
The various structures drawn for a molecule are called canonical or resonating structures.

RULES FOR DRAWING RESONATING STRUCTURES

As we have seen the one way of expressing the actual structure of a molecule containing delocalized bonds is to draw several possible structures and to assume that the actual molecule is a hybrid of them. These canonical forms have no existence except in our imaginations. The molecule does not rapidly shift between them. It is not the case that some molecules have one canonical form and some another. All the molecules of the substance have the same structure. The structure is always the same all the time and is a weighted average of all the canonical forms. In drawing canonical forms and deriving the true structures from them, we are guided by some simple rules, which are as follows.

1. All the canonical forms must be bonafide Lewis structures. For instance, none of them may have a carbon with five bonds.

2. The positions of the nuclei must be the same in all structures. This means that when we draw the various canonical forms, we cannot change the relative position of atoms but can change relative position of electron pairs.



The resonance interaction of chlorine with the benzene ring can be represented as above. In all structures explaining resonance, the sigma bonds are not involved, only the π or unshared electrons are put in different ways. This means that if we write one canonical form for a molecule, we can write the others by merely moving π and unshared electrons.

3. All atoms taking part in resonance i.e. covered by delocalized electrons, must lie in a plane or nearly so. This of course does not apply to atoms, which have the same bonding in all the canonical forms. The reason for planarity is maximum overlap of the p-orbitals.

4. All canonical forms must have the same number of unpaired electrons. Thus $^{\bullet}CH_2-CH=CH-\overset{\ominus}{C}H_2$ is a valid canonical form but $\dot{C}H_2-CH=CH-\dot{C}H_2$ is not a valid canonical form for 1,3-butadiene.

5. The energy of the actual molecule is lower than that of any canonical form or contributing form obviously. Therefore, delocalization is a stabilizing phenomenon.

6. All canonical forms do not contribute equally to the true molecule. Each form contributes in proportion to its stability, the most stable form contributing most. Thus, for ethylene, the form $\bar{C}H_2-\dot{C}H_2$ has such a high energy compared to $CH_2=CH_2$ that it essentially does not contribute at all. Equivalent canonical forms contribute equally. The greater the number of significant structures that can be written and the more nearly equal they are, the greater the resonance energy, other things being equal.

It is not always easy to decide relative stabilities of imaginary structures; the chemists are often guided by intuition. However the following rules may be helpful.

(a) Structures with more covalent bonds are ordinarily more stable than those with fewer.

(b) Stability is decreased by an increase in charge separation. Structures with formal charges are less stable than uncharged structures. Structures with more than two formal charges usually contribute very little. An especially unfavorable type of structure is one with two like charges on adjacent atoms.

(c) Structures that carry a negative charge on a more electronegative atom are more stable than those in which the charge is on a less electronegative atom. Also it is favorable to have positive charge, carried by low electronegative atom.

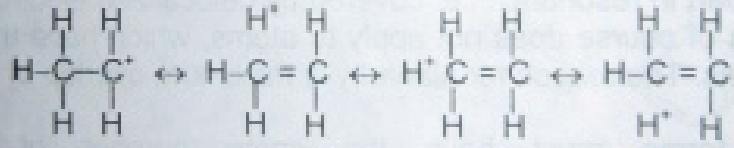
(d) Structures with octet of every atom being complete are more stable than any other structure.

T-1

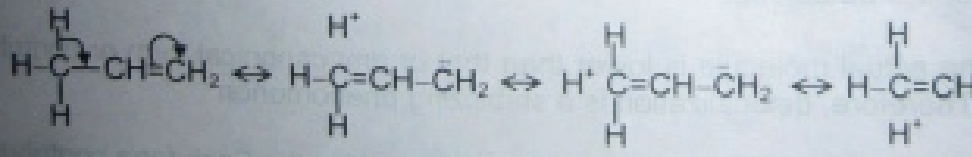
Draw resonating structure of $R-\overset{+}{C}=\ddot{O}$: and compare the stabilities of contributing structures.

7. HYPERCONJUGATION

This involves the conjugation between σ-electrons of a single carbon-hydrogen bond and the π-electron of the adjacent multiple bond. It is also called as no bond resonance because in the different canonical forms, no bond exists between carbon and H-atom of the alkyl group. For example, resonance structures of ethyl cation can be shown as follows.

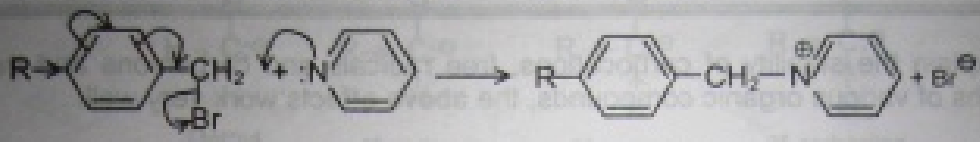


Hyperconjugation is also possible in alkenes and alkyl arenes. For example, for propene, it can be shown as follows,

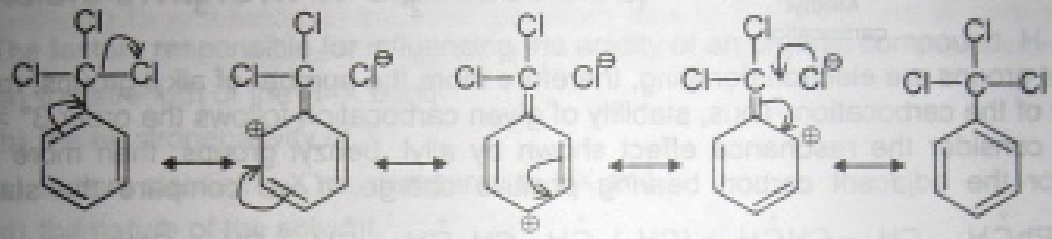


As we have seen, the inductive effect of alkyl groups is in the order $R_3C- > R_2CH- > RCH_2- > CH_3-$. This inductive order has been used satisfactorily to explain many phenomena like the dipole moments in the gas phase of $PhCH_3$, PhC_2H_5, $PhCH(CH_3)_2$ and $PhC(CH_3)_3$, which are 0.37, 0.58, 0.65 and 0.70 D respectively. However, in some reactions, the inductive order is reversed. For example, the rate of reaction of p-substituted benzyl bromide with pyridine in acetone (follows S_N2 pathway) is just opposite than that expected from the electron release by the inductive effect. That is, the methyl substituted compound reacted fast and the isopropyl

substituted compound reacted slower and the t-butyl substituted compound reacted slowest. The rate order for the R groups was Me– > CH_3CH_2– > isoPr– > t-Bu–.



Thus, the order of electron release is exactly the reverse of inductive effect of alkyl groups. Therefore, alkyl groups must also possess some other mechanism of electron release in which the order is Me– > CH_3CH_2– > isoPr– > t-Bu–. This effect is called as Hyperconjugation effect or Baker-Nathan effect (after its discoverer). In addition to the participation of hydrogen atom in hyperconjugation as shown above, chlorine atom also takes part in hyperconjugation as observed in trichloromethyl benzene as shown below. The hyperconjugation in alkyl groups is classified as +H while in trichloromethyl is classified as –H effect.



This explains the m-directing nature of $-CCl_3$ group.

Illustration 1

Question: **Explain the observed heat of hydrogenation of the following olefins.**

Olefin	Heats of hydrogenation in kcal/mole
$CH_2=CH_2$	31.0
$RCH=CH_2$	28.5
RCH=CHR (cis)	27.0
RCH=CHR (trans)	25.7

Solution: See the stability order according to the hyperconjugation theory.

RCH=CHR (trans) > RCH=CHR (cis) > $RCH=CH_2$ > $CH_2=CH_2$

Illustration 2

Question: **Explain the dipole moment order for the following compounds,**

$Ph–CH_3 < PhC_2H_5 < PhCH(CH_3)_2 < PhC(CH_3)_3$ which is contrary to the Baker Nathan's observation.

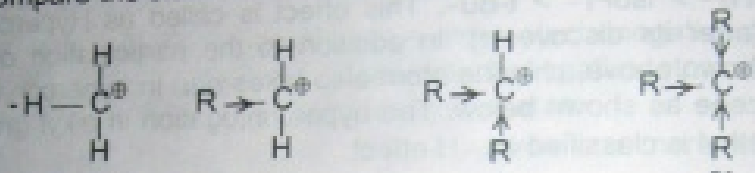
Solution: Only field effect of alkyl group in the gas phase explains the fact.

8. APPLICATION OF INDUCTIVE AND RESONANCE EFFECTS

To explain the stability of carbocations, free radicals and carbanions and the acidic and basic strengths of various organic compounds, the above effects work very well.

8.1 STABILITY OF CARBOCATIONS, FREE RADICALS AND CARBANIONS

Let us first compare the stabilities of following carbocations.



Methyl carbocation | 1° | 2° | 3°

Alkyl groups are electron donating, therefore more the number of alkyl groups, more will be the stability of the carbocation. Thus, stability of given carbocation follows the order 3° > 2° > 1° > CH_3. If we consider the resonance effect shown by allyl, benzyl groups, then more stability is observed for the adjacent carbon bearing positive charge. If we compare the stability then $(CH_3)_3\dot{C} > Ph\dot{C}H_2 > CH_2 = CH\dot{C}H_2 > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3 > CH_2 = \dot{C}H$. The observed anomaly for 3° cation with benzyl carbocation can only be explained if we consider the combined effect of hyperconjugation and inductive effect, which outweighs the sole resonance phenomenon shown by benzyl carbocation.

Illustration 3

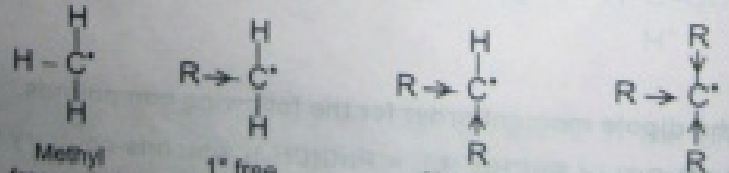
Question: **Which is more stable?**

$(CD_3)_3C^{\oplus}$ or $(CH_3)_3C^{\oplus}$

Solution: $(CD_3)_3C^{\oplus} + (CH_3)_3CH \rightleftharpoons (CD_3)_3C{-}H + (CH_3)_3C^{\oplus}$

Here K = 1.97 indicates that less hyperconjugation is observed in $(CD_3)_3C^{\oplus}$ compared to $(CH_3)_3C^{\oplus}$ because of D-atoms.

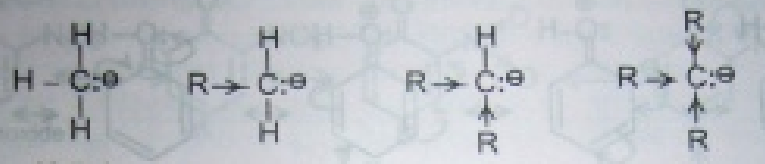
Now let us compare the stabilities of free radicals.



Methyl free radical | 1° free radical | 2° free radical | 3° free radical

As free radicals are electron deficient and R groups are electron donating, more the R groups more will be the stability of free radicals. Thus, stability order of free radicals is 3° > 2° > 1° > CH_3.

Finally, let us compare the stabilities of carbanions.



The stability of the carbanion decreases due to the presence of alkyl groups, as the negative charge on the carbon would be intensified. Thus, the order of stability of carbanion is $CH_3 > 1° > 2° > 3°$.

8.2 ACIDIC STRENGTH OF ORGANIC ACIDS

The factors responsible for influencing the acidity of an organic compound, H–X are

(a) the strength of the H–X bond

(b) the electronegativity of X

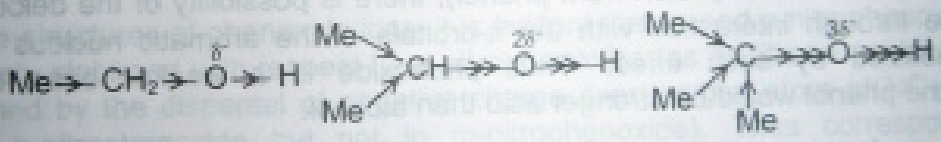
(c) factors stabilizing X^- as compared to HX and

(d) the nature of the solvent.

The most important factors among all is (c). Now let us see using any of these factors, how we can predict the order of acidic strength for organic acids.

(i) Alcohols

If we were to predict the order of acidic strength of ethanol, isopropanol and tertiary butanol, we can proceed as



As alkyl groups (methyl group) have a +I effect, the electron density at the oxygen atom will increase. More the number of alkyl groups, more will be the intensity of negative charge on oxygen. The greater the negative charge on the oxygen atom, the closer is the electron pair in the O–H bond driven to the hydrogen atom and consequently separation of a proton becomes increasingly difficult. Thus, the acidic strength of given alcohols will be in the order

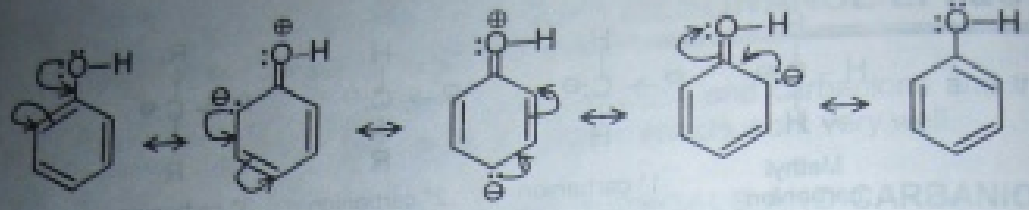
Ethanol > isopropanol > t-butanol

T-2

Of the ethanol and trifluoro ethanol which is more acidic?

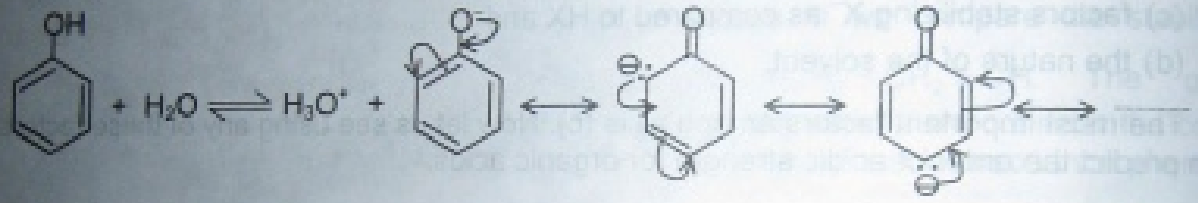
(ii) Phenols and other derivatives of phenols

(a) Because of resonance, the oxygen atom of the OH group acquires a positive charge and so proton release is facilitated.



It might be noted that since the carbon atom of C–OH group is sp^2 hybridised, it is more electron attracting than an sp^3 carbon atom (as in alcohols) and therefore there is an increased –I effect which facilitates proton release. But this inductive effect alone is not large enough to explain the increased acid strength of phenols as compared with alcohols.

(b) When phenol ionizes, the phenoxide ion is also a resonance hybrid, but it is more stabilised by resonance than is the unionized phenol molecule because of spreading of negative charge only. In the unionized molecule, unlike charges are spread and so is less stable.

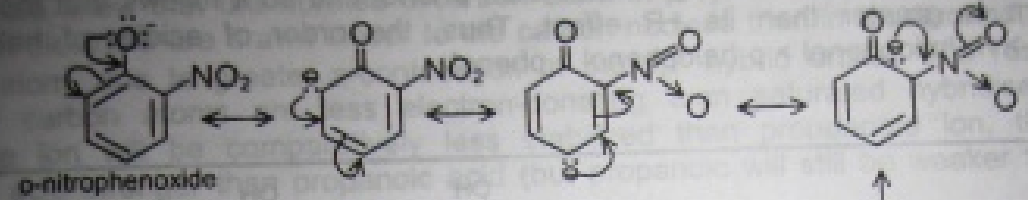


Phenols are stronger acids than alcohols. This is attributed to the fact that in phenoxide anion (obtained by the loss of proton from phenol), there is possibility of the delocalization of its negative charge through interaction with the π-orbitals of the aromatic nucleus while alkoxide cannot be stabilized by such effect. Thus phenoxide is a weaker base than alkoxide. Consequently, the phenol would be stronger acid than alcohol.

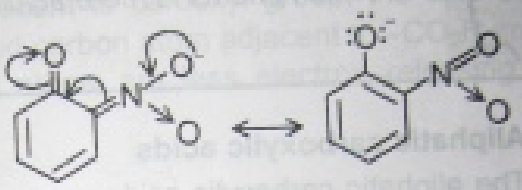
The effect of a ring substituent on the acid strength of phenol depends on whether the group is electron attracting or releasing, its ability to enter into resonance with the hydroxyl group, and its position. Effects in the o-position are similar to those in the p-position, but there are added complications due to the steric effect and to hydrogen bonding (when this is possible). Effects from meta position are altogether different from ortho and para position. In general, the presence of electron withdrawing groups in phenol increases its acidity while the presence of electron releasing groups decreases the acidity of phenol.

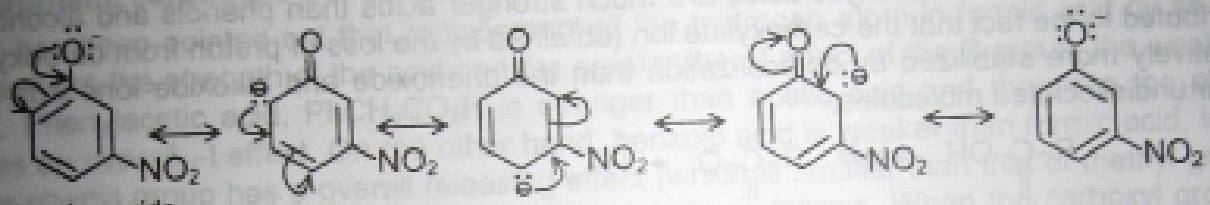
The methyl group decreases the acid strength of phenol from all ring positions. The methyl group is electron releasing and so release of a lone pair from oxygen (of the OH group in the unionized phenol or from the O^- in the phenoxide ion) into the ring is opposed. This results in diminished resonance in the contributing structures and consequently the phenoxide ion is more resonance stabilised with respect to phenol than is the methyl phenoxide ion with respect to methyl phenol. Hence, phenol is a stronger acid than all methyl phenols. The order of acidity of methyl phenols is phenol > m-methyl phenol > p-methyl phenol > o-methyl phenol.

Now, let us compare the acidic strength of o-, m- and p- nitrophenols. The corresponding phenoxide ions obtained from the three nitrophenols would be stabilized by delocalization as

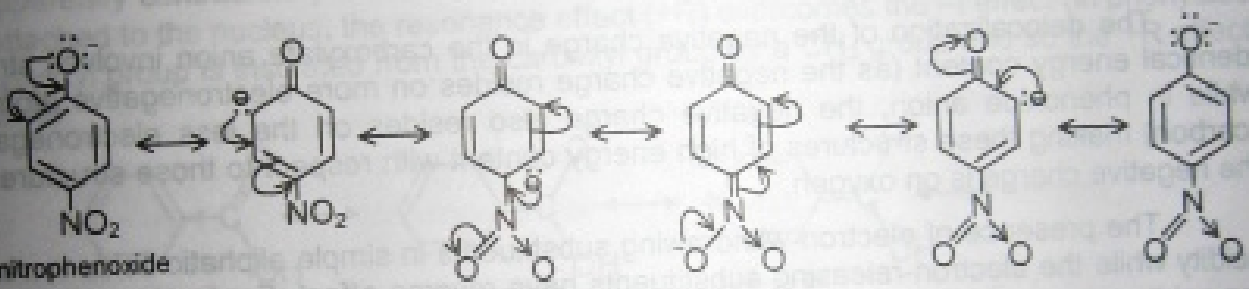


o-nitrophenoxide



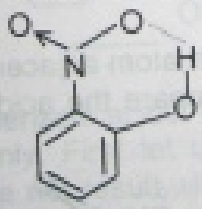


m-nitrophenoxide



p-nitrophenoxide

From the structures of phenoxide ions, it is evident that o- and p-nitrophenoxides are more extensively stabilized with respect to m-nitrophenoxide (as additional contributing structure is obtained by the dispersal of negative charge over oxygen atom of NO_2 group also in o- and p-nitrophenoxide but not in m-nitrophenoxide). Thus corresponding o- and p-nitrophenols are much stronger acids than m-nitrophenol. A meta-nitro group cannot enter into resonance with the hydroxyl group but can exert –I effect for this position. Hence, meta-nitrophenol is also stronger acid then phenol. Out of o- and p-nitrophenols, p-nitrophenol is slightly stronger than o-isomer as o-isomer is a bit stabilized by intramolecular hydrogen bonding, thus having a reduced tendency to release proton.



The order of acidic strength of the nitrophenols is

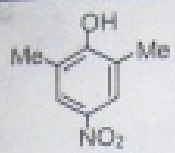
p-nitrophenol > o-nitrophenol > m-nitrophenol > phenol

The cumulative effect of three nitro groups in the 2,4,6 positions is shown by the fact that 2,4,6-trinitrophenols (picric acid) is a very strong acid.

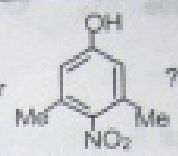
All the halophenols are stronger acids than phenol and so it follows that the –I effect of halogen atom is greater than its +R effect. Thus, the order of acidity of halophenols is o-halophenol > m-halophenol > p-halophenol > phenol.

T-3

Which phenol is more acidic,



or



?

(iii) Aliphatic carboxylic acids

The aliphatic carboxylic acids are much stronger acids than phenols and alcohols. This is attributed to the fact that the carboxylate ion (obtained by the loss of proton from carboxylic acid) is relatively more stabilized by delocalization than the phenoxide and alkoxide ions with respect to their undissociated molecules.

$$R-\underset{\underset{O}{\|}}{C}-OH \rightleftharpoons R-\underset{\underset{O}{\|}}{C}-O^- + H^+$$

The delocalization of the negative charge in the carboxylate anion involves structures of identical energy content (as the negative charge resides on more electronegative atom, oxygen) while in phenoxide anion, the negative charge also resides on the less electronegative atom (carbon) making these structures of high energy content with respect to those structures in which the negative charge is on oxygen.

The presence of electron-withdrawing substituents in simple aliphatic acids increases their acidity while the electron-releasing substituents have reverse effect. For instance, let us compare the acidic strength of fluoroacetic acid and acetic acid.

$$CH_3-\underset{\underset{O}{\|}}{C}-OH \rightleftharpoons CH_3 \rightarrow \underset{\underset{O}{\|}}{C}-O^- + H^+$$

$$F-CH_2-\underset{\underset{O}{\|}}{C}-OH \rightleftharpoons F \leftarrow CH_2 \leftarrow \underset{\underset{O}{\|}}{C}-O^- + H^+$$

The fluoroacetate ion is stabilized more due to strong –I effect of fluorine, with respect to acetate ion. Hence, fluroacetate ion is less basic than acetate ion, thereby making fluoroacetic acid stronger than acetic acid.

If there is a doubly bonded carbon atom adjacent to the carboxyl group, the acid strength is increased. This will be evident if we compare the acid strength of propanoic acid and propenoic (acrylic) acid.

$$CH_2=CH-CO_2H \rightleftharpoons CH_2=\overset{\alpha}{C}H-\underset{O^-}{\overset{O}{\overset{\|}{C}}} + H^+$$

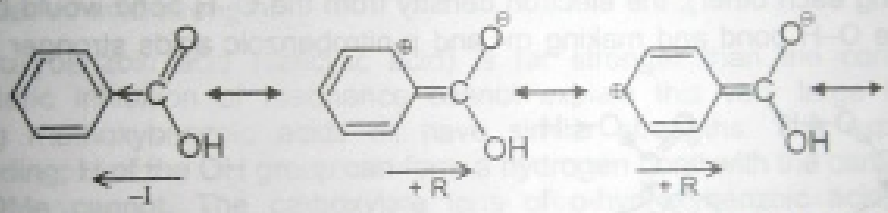
$$CH_3-CH_2-CO_2H \rightleftharpoons CH_3-\overset{\alpha}{C}H_2-\underset{O^-}{\overset{O}{\overset{\|}{C}}} + H^+$$

As we know that unsaturated α-carbon atom in propenoate ion is sp^2 hybridised, which means that electrons are drawn closer to the carbon nucleus than in a saturated, sp^3 hybridised α-carbon atom, due to greater s-contribution in the sp^2 hybrid orbital. The result is that sp^2 hybridised carbon atoms are less electron-donating than saturated hybridised ones, thus, propanoate ion will be comparatively less stabilized than propenoate ion, thereby making propenoic acid stronger than propanoic acid (but propanoic will still be weaker than methanoic acid).

If there is a triple bonded carbon atom adjacent to carboxyl group, the acid strength is more with respect to the presence of a doubly bonded carbon atom adjacent to $-CO_2H$ group. This is attributed to the fact that sp hybridized carbon atoms are less electron-releasing than sp^2 hybridized carbon atoms.

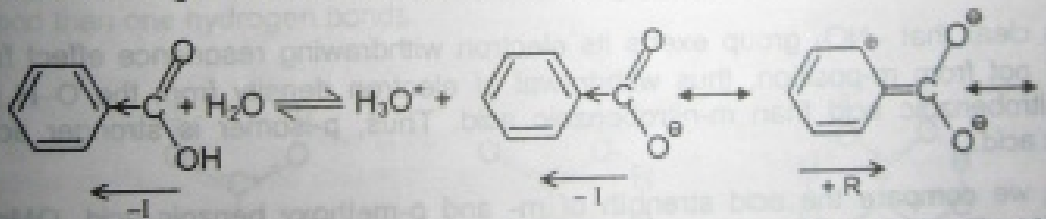
(iv) Aromatic carboxylic acids

It has been pointed out that replacement of the hydrogen atom in formic acid by an alkyl group weakens the strength of the acid and the greater the +I effect of the R group, the weaker is the acid. Phenylacetic acid, $PhCH_2CO_2H$ is stronger than acetic acid and therefore the phenyl group has an overall –I effect. On the other hand, benzoic acid is weaker than formic acid. In this case, the phenyl group has a overall releasing effect (which is smaller than that of methyl group). These apparently contradictory results may be explained as follows. When the carboxyl group is directly attached to the nucleus, the resonance effect (+R) overcomes the –I effect (in phenylacetic acid the phenyl group is insulated from the carboxyl group by a CH_2 group and so the +R effect is not possible):

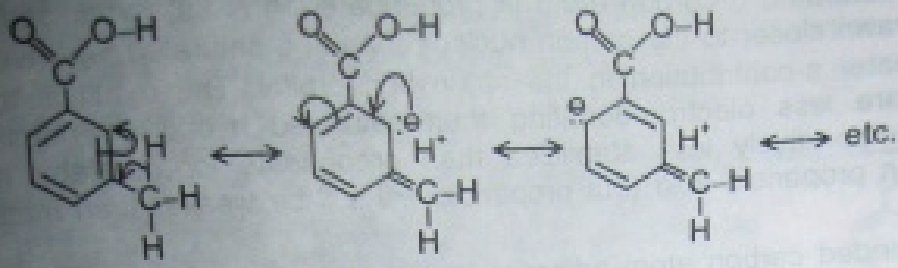


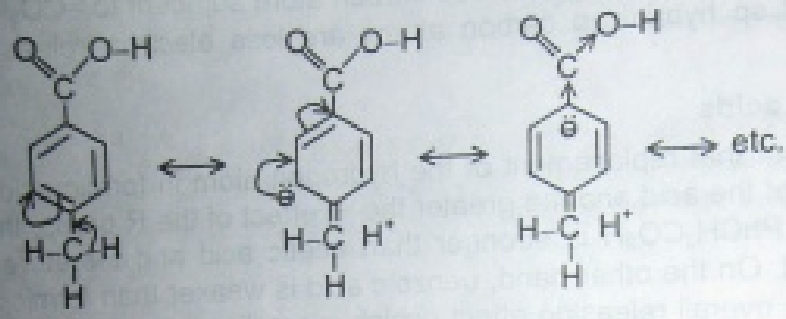
This prevents to a large extent, the lone pair on the O-atom of the –OH group from entering into resonance with the –CO group. The result is a smaller positive charge on the O-atom of the –OH group and so proton release is more difficult than in formic acid. The fact that benzoic acid is stronger than acetic acid means that [–I +(+R)] < +I of the methyl group.

The same arguments may be applied to ionised benzoic acid.



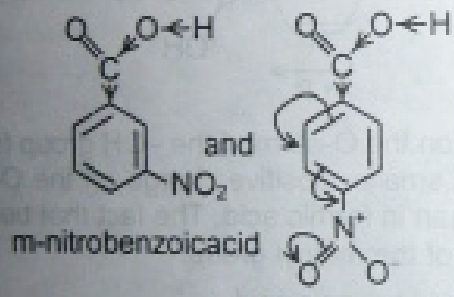
Now let us consider substituted benzoic acids. At this point, we will consider the effect of substituents from m- and p-positions only. First let us take methyl substituted benzoic acids. As the methyl group has +I effect, so the net result will be to increase the +R effect in the m- or p-tolyl group. Since, the inductive effect decreases with distance, so the +I effect of CH_3 from para position would be less than the +I effect of CH_3 group from meta position. Thus, the electron density in the O–H bond of m-methyl benzoic acid would be greater than that in p-methyl benzoic acid. Accordingly, the p-isomer should be more acidic than the m-isomer. But in real practice, the order is reverse. Actually, we have ignored the hyperconjugation effect of CH_3 group. Due to hyperconjugation effect of CH_3 in p-isomer, the electron density in the O–H bond would be increased greatly with respect to that in m-isomer.





Thus, the release of proton is facilitated easily in m-isomer than in p-isomer.

Secondly, let us take nitro substituted benzoic acids. As the $-NO_2$ group exerts –I and –R effect (both reinforcing each other), the electron density from the O–H bond would be withdrawn, thus destabilizing the O–H bond and making m- and p-nitrobenzoic acids stronger than benzoic acid.

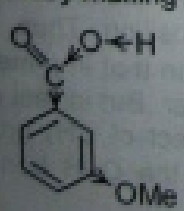


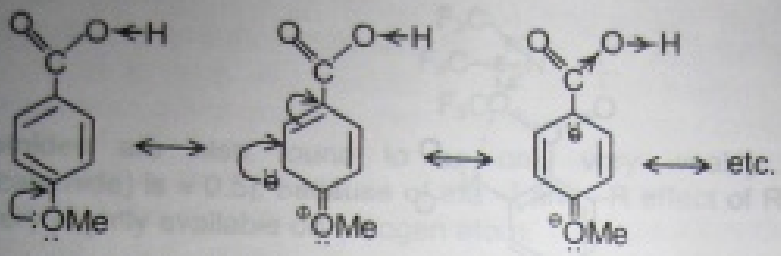
m-nitrobenzoicacid

p-nitrobenzoicacid

As it is clear that $-NO_2$ group exerts its electron withdrawing resonance effect from the p-position and not from m-position, thus withdrawal of electron density from the O–H bond is greater in p-nitrobenzoic acid than m-nitrobenzoic acid. Thus, p-isomer is stronger acid than m-nitrobenzoic acid.

Thirdly, we compare the acid strength of m- and p-methoxy benzoic acid. OMe group exerts –I and +R effects. The electron releasing resonance effect (+R) is operative in p-methoxy benzoic acid and not in m-methoxy benzoic acid while – I effect is operative in both the isomers. Thus, the electron density is greatly increased in the O–H bond in p-isomer than in m-isomer, thereby making m-isomer stronger acid than p-isomer.





The ortho-effect. This is a special effect that is shown by o-substituents, but is not necessarily just a steric effect. Examination shows that, irrespective of the polar type, nearly all o-substituted benzoic acids are stronger than benzoic acid.

As we have seen that benzoic acid is a resonance hybrid and so the carboxyl group is coplanar with the ring. An o-substituent tends to prevent this coplanarity. Thus, resonance is diminished (or prevented) and so the O-atom of the –OH group has a greater negative charge, resulting in increased acid strength. It follows from this, that greater the steric inhibition of resonance, the stronger is the acid. Support for this is the following order of strengths of substituted benzoic acids.

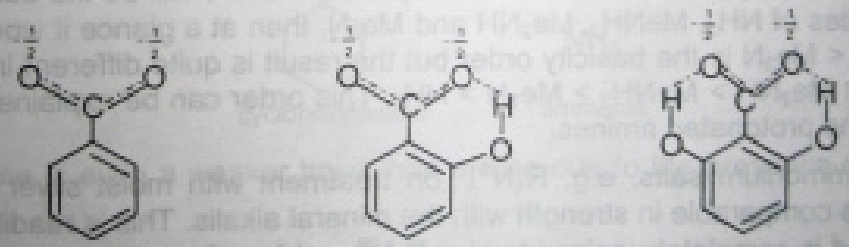
2, 6-di-Me > 2-t-Bu > 2-Me

Here again, if we consider the stability of the anion, steric inhibition of resonance prevents the +R effect of the ring coming into operation and since this weakens acid strength, its absence results in increased acid strength.

o-hydroxybenzoic acid (salicylic acid) is far stronger than the corresponding m- and p-isomers. Steric inhibition of resonance cannot explain this very large increase, since the corresponding methoxybenzoic acids all have similar strengths. The explanation offered is hydrogen bonding; H of the OH group can form a hydrogen bond with the carboxyl group, whereas the Me of OMe cannot. The carboxylate ions of o-hydroxybenzoic acids are stabilised by intramolecular hydrogen bonding and support for this is given by the following order of acid strength,

2, 6-di-OH > 2-OH > benzoic acid

It can be seen that two hydrogen bonds would be expected to bring about more stabilization than one hydrogen bonds.



The much greater strength of o-nitrobenzoic acid as compared with that of its m- and p-isomers may also be explained in a similar manner.

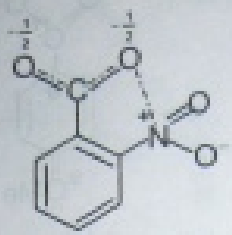
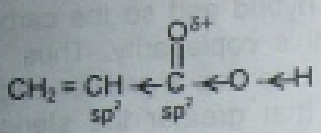


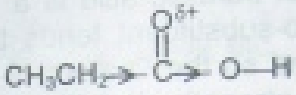
Illustration 4

Question: **Explain why acrylic acid is stronger acid than propionic acid?**

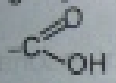
Solution:



Acrylic acid



Propionic acid

If we look at these two acids, electron withdrawing effect of sp^2 carbon adjacent to carbonyl group in acrylic acid is observed and consequent strong polarization of O–H bond in  form takes place. Ethyl group in propionic acid has +I effect to the carboxyl group reducing the partial positive character of C-atom in group. Therefore, less polarization of O–H takes place.

T-4

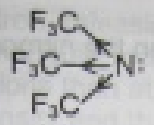
Account for the fact that salicylic acid, o-$HOC_6H_4CO_2H$ is a stronger acid than o-$CH_3OC_6H_4CO_2H$.

8.3 BASIC STRENGTH OF ORGANIC BASES

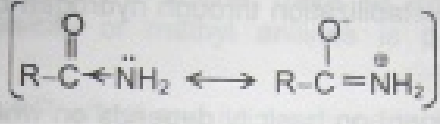
Strength of bases is related to the ease of accepting a proton, which in turn depends on the availability of electron pair on the nitrogen atom (or some other basic atom). More is the availability of electron pair, more easily the proton will be accepted and more will be the basic strength. If we compare the basicities of NH_3, $MeNH_2$, Me_2NH and Me_3N, then at a glance it would seem like $NH_3 < MeNH_2 < Me_2NH < Me_3N$ is the basicity order but the result is quite different in aqueous media. The correct order is $Me_2NH > MeNH_2 > Me_3N > NH_3$. This order can be explained considering the solvation effect of the protonated amines.

Tetra-alkylammonium salts, e.g. $R_4N^{\oplus}I^-$ on treatment with moist silver oxide (AgOH) to yield basic solutions comparable in strength with the mineral alkalis. This is readily understandable as $R_4N^{\oplus}\ ^-OH$ formed is completely ionized to give $R_4N^{\oplus}$ and free OH^-.

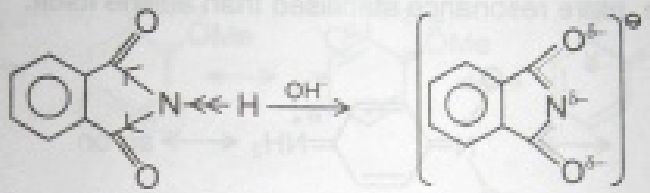
The effect of introducing electron withdrawing groups, e.g. Cl, NO_2, close to a basic centre decreases the basicity, due to their electron withdrawing inductive effect. Thus the amine Tris (trifluoromethyl) amine is found to be virtually non-basic due to the presence of three powerful electron withdrawing CF_3 groups.



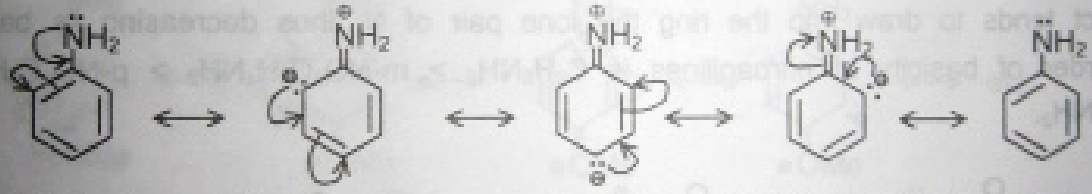
The amides are also found to be only very weakly basic in water [pK_a for ethanamide(acetamide) is = 0.5], because of the –I and –R effect of RCO group which makes the electron pair very slightly available on nitrogen atom.



If two C = O groups are present, the resultant imides often become sufficiently acidic to form alkali metal salts. For example, benzene-1,2-dicarboximide is not basic but is acidic in nature because of the presence of two electron withdrawing CO groups.



In aniline, owing to resonance, the lone pair of electrons on the nitrogen atom is less available for coordinating with a proton and at the same time, small positive charge on the nitrogen atom would tend to repel a proton. Alternatively, since there are more resonating structures possible for aniline itself than for the cation $C_6H_5\dot{N}H_3$, the former will be stabilized with respect to the latter.

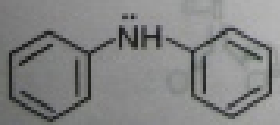


Aniline is a weaker base than ammonia or cyclohexylamine. It is because of the fact that the electron pair on nitrogen is involved in delocalization, making it less available for donation.

cyclohexylamine

ammonia

Diphenylamine is even a weaker base than aniline due to the presence of another phenyl group



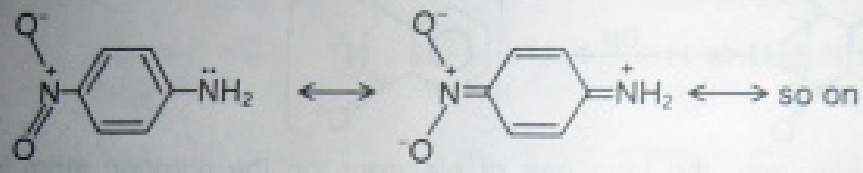
and triphenylamine (Ph_3N) is not basic at all by ordinary standards.

Introduction of alkyl group (like Me) on the nitrogen atom of aniline results in small increase in the basic strength.

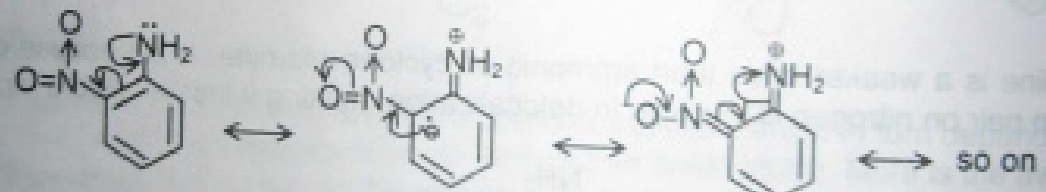
$$C_6H_5NH_2 < C_6H_5NH_2Me < C_6H_5NMe_2$$

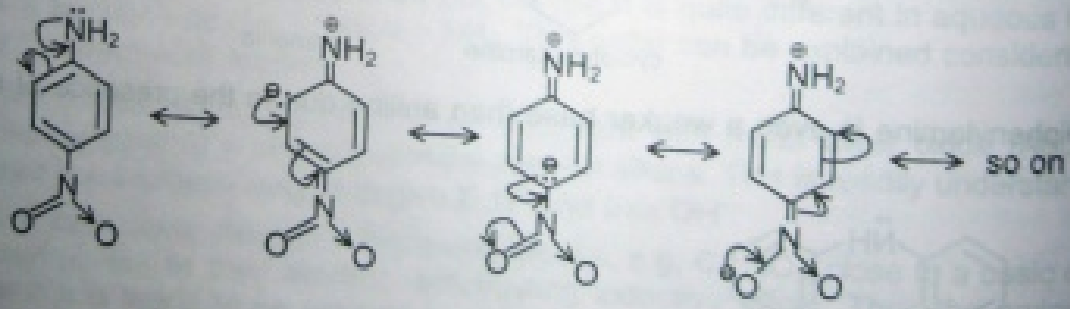
Unlike such introduction in aliphatic amines, this small increase in basic strength is progressive, indicating that cation stabilization through hydrogen-bonded solvation, here has less influence on the overall effect.

The effect of a ring substituent on basicity depends on whether the substituent is electron attracting or releasing, its ability to enter into resonance with the amino-group and its position. All the nitroanilines are weaker bases than aniline. The nitro-group has a strong –R effect and o- and p-nitroaniline are therefore, more resonance stabilised than aniline itself.



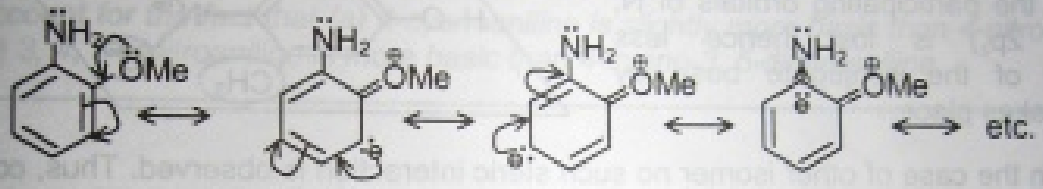
A m-nitro group cannot enter into resonance with the amino-group, but nevertheless m–nitroaniline is a much weaker base than aniline. In this case, nitro-group has a strong –I effect. This –I effect tends to draw into the ring the lone pair of N, thus decreasing its basicity. Thus, the order of basicity of nitroanilines is $C_6H_5NH_2$ > m-$NO_2C_6H_4NH_2$ > p-$NO_2C_6H_4NH_2$ > o-$NO_2C_6H_4NH_2$.

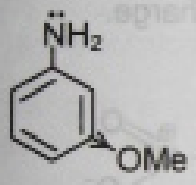


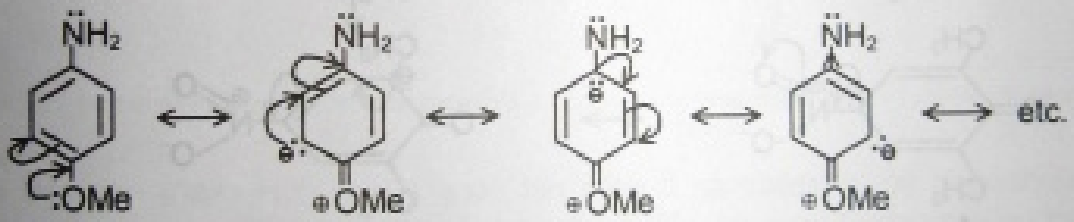


When the ring contains an electron releasing group, this reduces resonance of the NH_2 group with the ring and consequently should increase basicity. The methyl group raises the electron density more at the o- and p-positions than at the m-position. Thus, the carbon atom para to the methyl group has a high electron density and the lone pair on the nitrogen atom is therefore prevented to some extent from entering into resonance with the ring. A methyl group raises the electron density at the m-position only to a very small extent. Hence, resonance with the ring of NH_2 group at this position is prevented less than for the p-position. Consequently, a methyl group in the ring increases the basicity of the aniline, more so from the p-position than from the m-position. Thus, order of basicity of methyl anilines is $p\text{-}CH_3C_6H_4NH_2 > m\text{-}CH_3C_6H_4NH_2 > C_6H_5NH_2 > o\text{-}CH_3C_6H_4NH_2$.

The p-OMe group has a +R effect and its presence increases basicity. In the m-position it can exert only a –I effect and this decreases the basicity. The order of basicity of methoxy anilines is $p\text{-}CH_3OC_6H_4NH_2 > C_6H_5NH_2 > o\text{-}CH_3OC_6H_4NH_2 > m\text{-}CH_3OC_6H_4NH_2$.





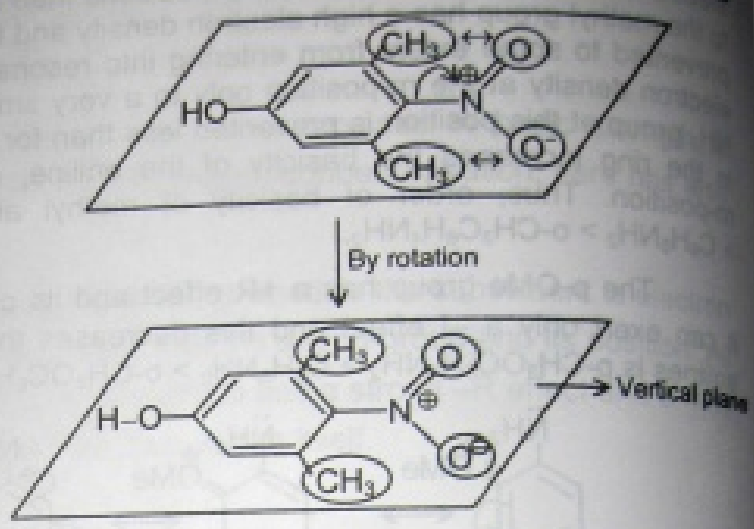


T-5

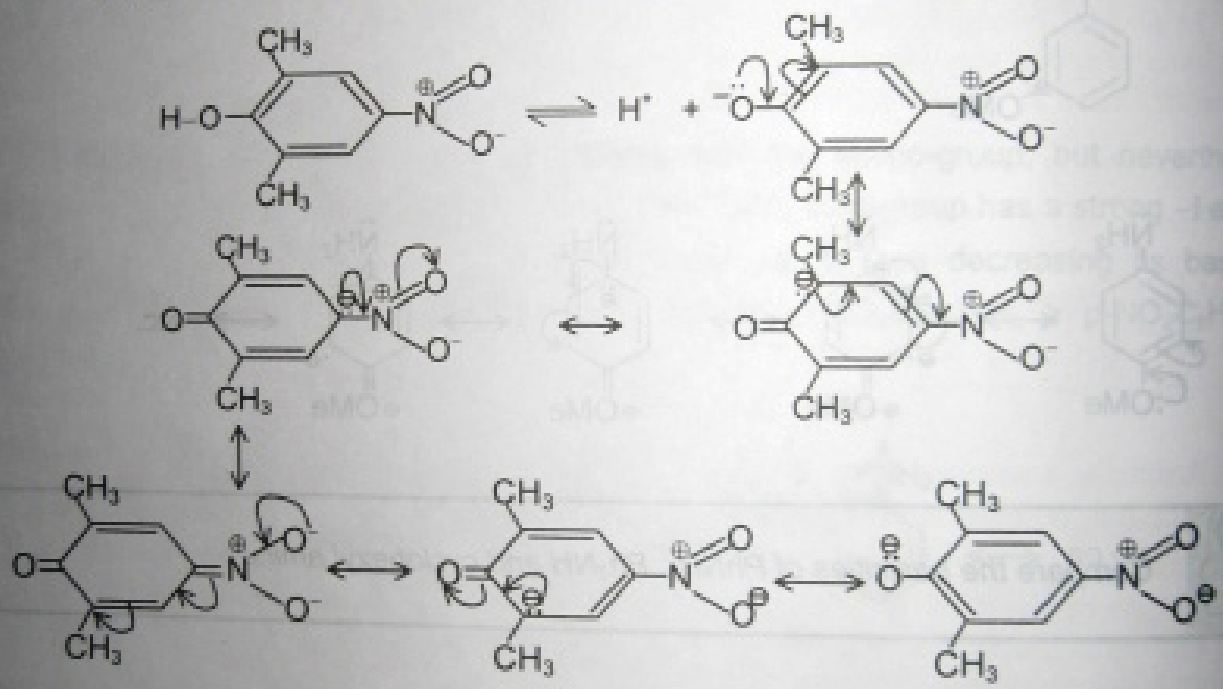
Compare the basicities of $PhNH_2$, Ph_2NH and cyclohexyl amine.

9. STERIC INHIBITION OF RESONANCE

We find many a times that due to steric reasons (the repulsion between the bulky groups), the resonance phenomenon is hindered, which might otherwise be possible due to loss of planarity of the group. For example, let us compare the acidity of 3, 5-dimethyl-4-nitrophenol and 2, 6-dimethyl-4-nitrophenol. The explanation is neighbouring methyl groups will repel the bulky nitro group and consequent planarity of the participating orbitals of N, (which is $2p_z$) is lost hence less stabilization of the conjugate base by resonance takes place.

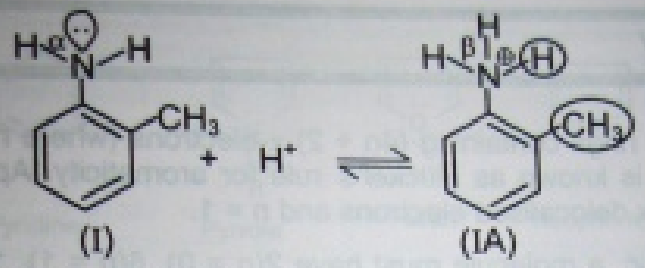


But in the case of other isomer no such steric interaction is observed. Thus, corresponding stability of conjugate base through extensive delocalisation of negative charge.



Steric reasons also play important role in determining basicity of aromatic amines like 3, 5-dimethyl-4-nitroaniline (pK_a = 2.49), 2, 6 dimethyl-4-nitroaniline (pK_a = 0.95). On the same argument, it can be said that lone pair of $-NH_2$ group cannot go to the apparently available $-NO_2$ group by conjugation.

Another interesting case arises with the observed basicities of o-methyl aniline (I), m-methyl aniline (II) and p-methyl aniline (III). By the diminishing +I effect behaviour of $-CH_3$ groups (I) > (II) > (III) order should have been anticipated. But the correct order is (III) > (II) > (I). This can be anticipated by the stability of conjugate acid, which is found to be less stable because of steric repulsion, experienced by proton (extra) and existing $-CH_3$ group at ortho position.



(I) (IA)

In (I), $\alpha < 109°28'$, so less steric repulsion was experienced by $-CH_3$ and H of NH_2 group. But once protonated, $\beta = 109°28'$ i.e. the groups spread and consequently the crowding with the CH_3 occurs.

T-6

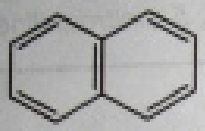
Account for the fact that (a) 4-cyanoaniline is slightly more basic than 4-nitroaniline and (b) 3, 4, 5-trinitroaniline is more basic than 4-cyano-3, 5-dinitroaniline.

10. AROMATICITY

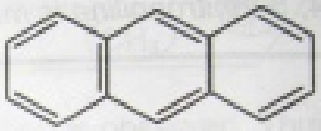
Planar monocyclic rings containing (4n + 2) π-electrons (where n = 0, 1, 2, 3, and so on), should be aromatic. This is known as Hückel's rule for aromaticity. Applying this rule, benzene and its derivatives have six delocalised electrons and n = 1.

Thus to be aromatic, a molecule must have 2(n = 0), 6(n = 1), 10(n = 2) π-electrons in a closed π-orbital loop. Another requirement for aromaticity is planarity of the ring. If the ring is not planar, overlap of p-orbitals is diminished or prevented, then compound will not be aromatic.

Derivatives of benzene are aromatic as they fulfill both the conditions. Molecules having two or more benzene rings fused together are called polycyclic benzenoid aromatic hydrocarbons. For example, naphthalene, anthracene etc.

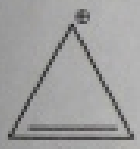


Naphthalene, n = 2
Number of π-electrons = 10



Anthracene, n = 3
Number of π-electrons = 14

Non-benzenoid aromatic compounds are those which contain a ring that is not six membered. For example, cyclopentadienyl anion, cyclopropenium cation, tropylium cation etc.



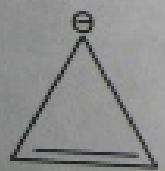
Cyclopropenium cation
(n = 0)

Cyclopentadienyl anion
(n = 1)

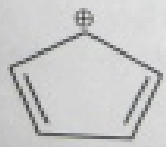
Tropylium cation (Cycloheptatrienyl cation)
(n = 1)

Cyclopentadiene is not aromatic as it does not obey (4n + 2) Huckel's rule and also the π-electrons cannot be delocalized because of the tetrahedral CH_2 group. When a proton is removed from this carbon atom, it becomes sp^2 hybridised and thus delocalization is permitted. Thus, this anion becomes aromatic in nature. Cycloheptatriene has six π-electrons but the CH_2 group prevents delocalization. When a hydride ion is removed from this carbon atom, a vacant p-orbital is created, which makes the carbon atom sp^2 hybridised and thus cation becomes aromatic in nature.

Cyclic conjugated compounds, which possess only 4n electrons, do not satisfy the Huckel rule and are anti-aromatic in nature.



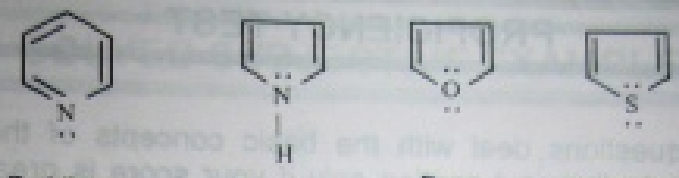
Cyclopropenium anion



Cyclopentadienyl cation

Tropylium anion

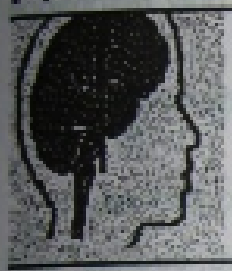
In cyclic compounds, when an element other than carbon is present in the ring, they are called heterocyclic compounds. They are aromatic in nature because of fulfilling both the conditions.



Pyridine Pyrrole Furan Thiophene

In pyrrole, furan and thiophene, the lone pairs are actually in sp^3 hybrid orbitals to form the aromatic sextet (4n + 2) π-electron. In pyridine, the lone pair is in sp^2 hybrid orbital, which is not involved in delocalization. Thus, pyridine also has 6 π-electrons and is aromatic in nature.

T-7



Why are the following substances not aromatic?

(a)
(cycloheptatriene)

(b)
(3-methylene-1, 4-cyclohexadiene)

(c)
(cyclobutadiene)

PROFICIENCY TEST

The following 10 questions deal with the basic concepts of this section. Answer the following briefly. Go to the next section only if your score is greater than or equal to 8. Do not consult the study material while attempting the questions.

1. True/False. The $-OCH_3$ group belongs to +I group.
2. True/False. Resonance and tautomerism refer to one and the same phenomenon.
3. True/False. The $-OH$ and $-NH_2$ groups attached to aromatic ring have only resonance effects.
4. True/False. In a carboxylic acid RCOOH, the factor stabilising the carboxylate anion, $RCOO^-$, relative to RCOOH increases the acidity of the acid.
5. True/False. Inductive effect is independent of the distance between the two centres.
6. True/False. The resonance stabilisation of formate anion makes formic acid, stronger acid than acetic acid.
7. True/False. The stability of carbocations follows the order,

$$\overset{+}{C}H_3 > CH_3\overset{+}{C}H_2 > (CH_3)_2\overset{+}{C}H > (CH_3)_3\overset{+}{C}$$

8. True/False. In acylium ion, the structure $R—C \equiv \overset{+}{O}$ is more stable than $R—\overset{\oplus}{C}=O$.
9. True/False. The order of basicity of nitroanilines is $m\text{-}NO_2C_6H_4NH_2 > p\text{-}NO_2C_6H_4NH_2 > o\text{-}NO_2C_6H_4NH_2$.
10. True/False. Pyridine is an aromatic compound but pyrrole is not.

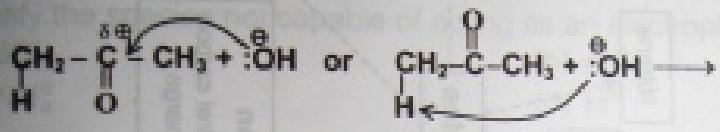
ANSWERS TO PROFICIENCY TEST

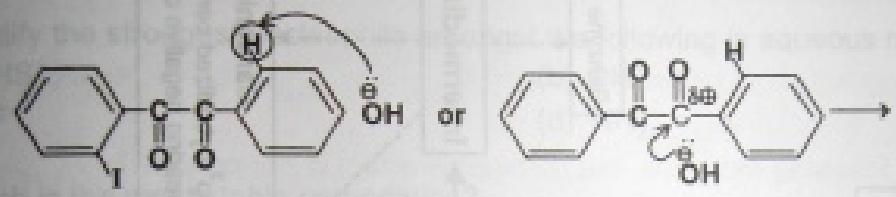
1. False
2. False
3. False
4. True
5. False
6. True
7. False
8. True
9. True
10. False

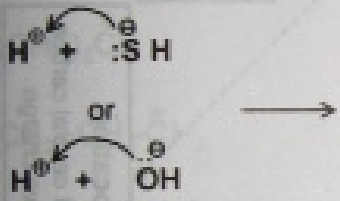
SOLVED SUBJECTIVE EXAMPLES

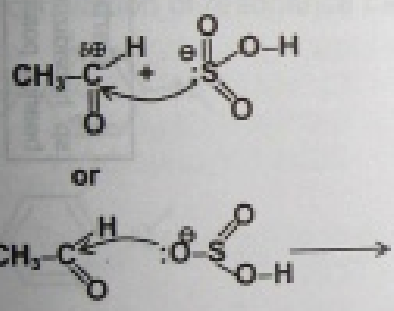
Example:

State which interactions are preferable and write the probable products of the following reactions.

(i) 

(ii) 

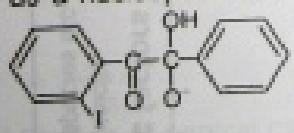
(iii) 

(iv) 

Solution:

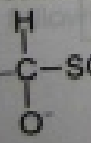
(i) As OH^- is a hard base it will prefer to abstract proton, which is a hard acid in this situation. The product is $^-CH_2COCH_3$ in equilibrium with CH_3COCH_3 and OH^-

(ii) Here OH^- is acting as a nucleophile as there is no acidic hydrogen available in the molecule.

The product is thus  in equilibrium with the reactants.

(iii) OH^- is a hard base but SH^- is a soft base. Obviously OH^- will prefer to bind with proton (H^+) more readily than HS^-. The product is H_2O at equilibrium.

(iv) S^- is a soft base. Hence, it will prefer to attack the soft acid $C^{\delta\oplus}$ of carbonyl carbon.

The product is  in equilibrium with the reactants.

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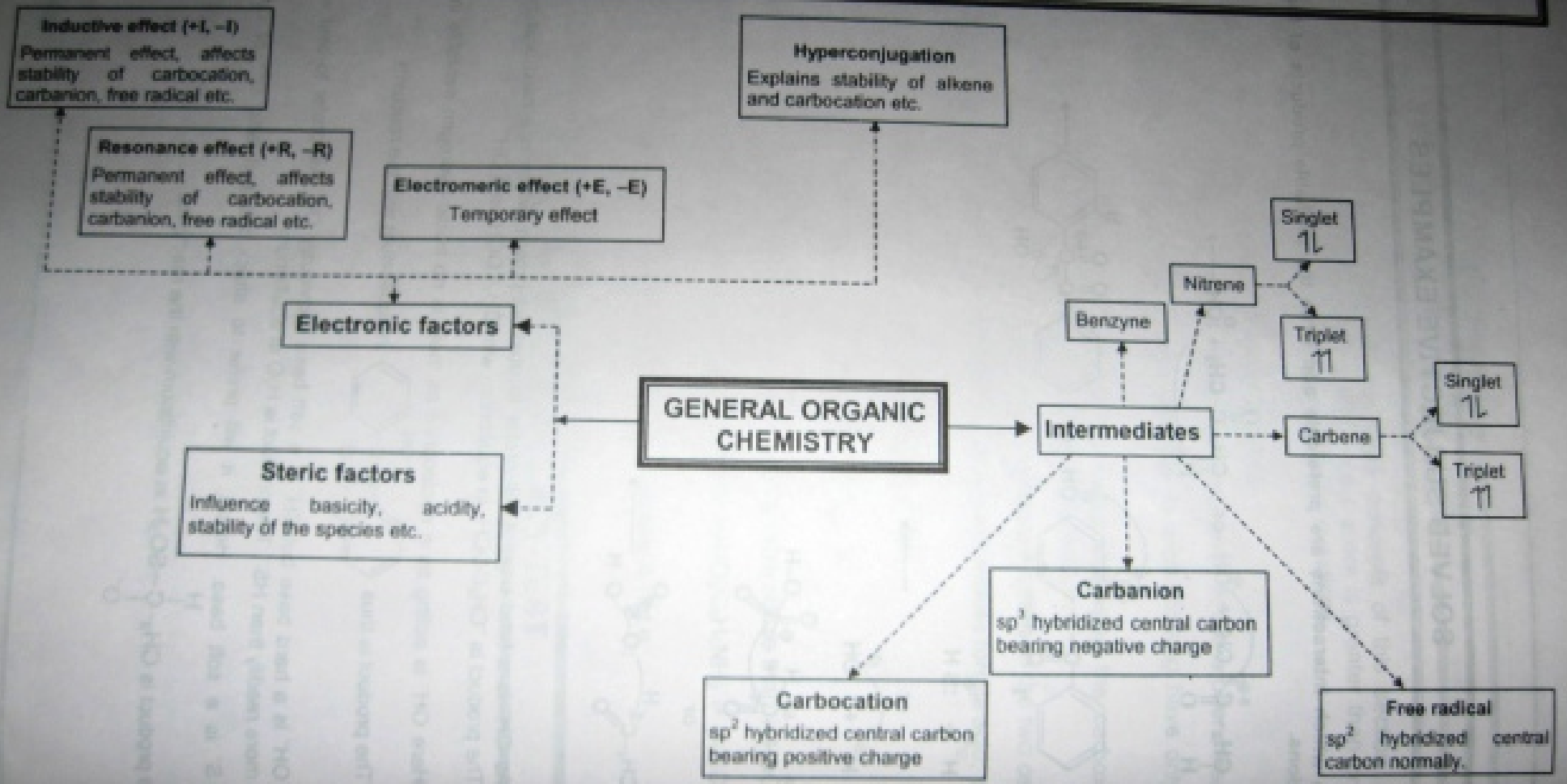
MIND MAP

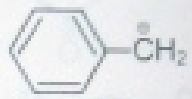

Inductive effect (+I, –I)
Permanent effect, affects stability of carbocation, carbanion, free radical etc.
Resonance effect (+R, –R)
Permanent effect, affects stability of carbocation, carbanion, free radical etc.
Electromeric effect (+E, –E)
Temporary effect
Hyperconjugation
Explains stability of alkene and carbocation etc.
Electronic factors
Steric factors
Influence basicity, acidity, stability of the species etc.
GENERAL ORGANIC CHEMISTRY
Intermediates
Benzyne
Nitrene
Singlet
Triplet
Carbene
Singlet
Triplet
Carbanion
sp3 hybridized central carbon bearing negative charge
Carbocation
sp2 hybridized central carbon bearing positive charge
Free radical
sp2 hybridized central carbon normally.

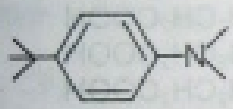
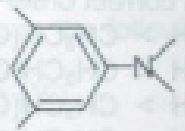
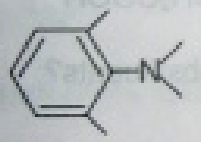
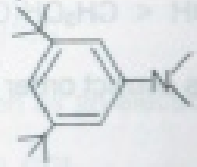
EXERCISE – I

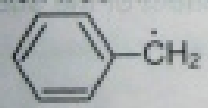
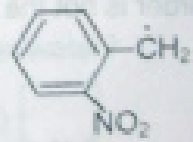
OBJECTIVE PROBLEMS WITH ONLY ONE CHOICE CORRECT

1. Identify the species not capable of acting as an electrophile.
(a) BCl_3
(b) $AlCl_3$
(c) $NH_4^{\oplus}$
(d) $H^{\oplus}$

2. Identify the strongest nucleophile amongst the following in aqueous medium.
(a) HS^-
(b) OH^-
(c) F^-
(d) NH_2^-

3. Which is the most stable carbocation?
(a) $(CH_3)_2\overset{\oplus}{C}H$
(b) 
(c) $CH_2=CH-\overset{\oplus}{C}H_2$
(d) $(CH_3)_2\overset{\oplus}{C}$

4. Steric inhibition of resonance can be expected in
(a) 
(b) 
(c) 
(d) 

5. Which free radical is the most stable one?
(a) 
(b) 
(c) $(CH_3)_3\dot{C}$
(d) $(CH_3)_2\dot{C}H$

6. In $(t\text{-}Bu)_3\dot{C}$, the hybridization of central carbon atom is
(a) sp
(b) sp^2
(c) sp^3
(d) none of these

7. Which one of the following group shows maximum –I effect?
(a) $NH_3^{\oplus}$
(b) $NH_2Me^{\oplus}$
(c) $NHMe_2^{\oplus}$
(d) $NMe_3^{\oplus}$

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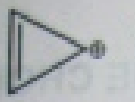
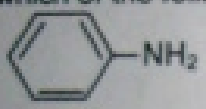
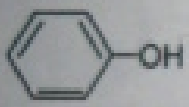
8. Anti-aromaticity appears when the compound has
(a) 4n π-electrons
(b) (4n + 1) π-electrons
(c) (4n + 2) π-electrons
(d) (4n + 3) π-electrons

9. The cyclopropenyl cation,  is
(a) aromatic
(b) anti-aromatic
(c) non-aromatic
(d) non planar

10. The cyclopentadienyl cation, is
(a) aromatic
(b) anti-aromatic
(c) non-aromatic
(d) none of these

11. In which of the following molecule, the resonance effect is not present?
(a) 
(b)
(c) 
(d)

12. Which of the following is correct order regarding the acidity of carboxylic group?
(a) $CH_3CH_2CH(Cl)COOH > CH_3CH(Cl)CH_2COOH > ClCH_2CH_2CH_2COOH$
(b) $CH_3CH_2CH(Cl)COOH < CH_3CH(Cl)CH_2COOH < ClCH_2CH_2CH_2COOH$
(c) $CH_3CH_2CH(Cl)COOH > CH_3CH(Cl)CH_2COOH < ClCH_2CH_2CH_2COOH$
(d) $CH_3CH_2CH(Cl)COOH < CH_3CH(Cl)CH_2COOH > ClCH_2CH_2CH_2COOH$

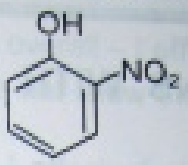
13. Which of the following is correct order regarding –I effect of the substituents?
(a) $-NR_2 > -OR > -F$
(b) $-NR_2 < -OR < -F$
(c) $-NR_2 > -OR < -F$
(d) $-NR_2 < -OR > -F$

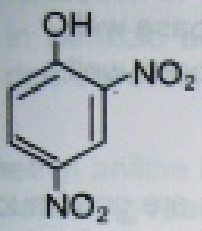
14. Which of the following order is not the correct order regarding –I effect of the substituents?
(a) $-I < -Cl < -Br < -F$
(b) $-NR_2 < -\overset{\oplus}{O}R_2$
(c) $-NR_2 < -OR < -F$
(d) $-SR < -OR < -\overset{\oplus}{O}R_2$

15. Which of the following is correct order regarding the acidity of carboxylic acids?
(a) $(CH_3)_3CCOOH > (CH_3)_2CHCOOH > CH_3CH_2COOH$
(b) $(CH_3)_3CCOOH > (CH_3)_2CHCOOH < CH_3CH_2COOH$
(c) $(CH_3)_3CCOOH < (CH_3)_2CHCOOH > CH_3CH_2COOH$
(d) $(CH_3)_3CCOOH < (CH_3)_2CHCOOH < CH_3CH_2COOH$

16. Which of the following compound has the highest pK_a value?

(a)

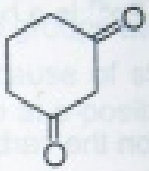
(b) 

(c) 

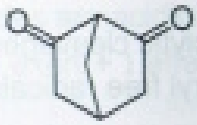
(d)

17. Which one of the following compound would you expect to be the strongest carbon acid?

(a) $CH_2(COOC_2H_5)_2$

(b) 

(c) $CH_3COCH_2COOC_2H_5$

(d) 

18. Which is the most stable singlet carbene among the following?

(a) $\ddot{C}F_2$

(b) $\ddot{C}Cl_2$

(c) $\ddot{C}Br_2$

(d) $\ddot{C}I_2$

19. Which of the following species cannot function as an electrophile?

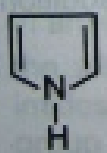
(a) HCl

(b) $\ddot{C}Cl_2$

(c) SiF_4

(d) $CH_2{=}CH_2$

20. Which of the following is the strongest base in water?

(a) 

(b)

(c)

(d)

EXERCISE – II

OBJECTIVE QUESTIONS WITH ONE OR MORE THAN ONE CHOICE CORRECT

1. Which of the following statements are correct?
(a) Soft acid binds soft base well.
(b) Soft acid binds hard base well.
(c) Hard acid binds hard base well.
(d) Hard acid binds soft base well.

2. Identify the correct statements.
(a) Soft acids are species, which are easily oxidisable and soft bases are good nucleophiles.
(b) Hard acids are not easily oxidisable and hard bases are strong bases.
(c) Hard acids have higher electronegativity while soft acids have lower electronegativity.
(d) Fe^{3+} is a soft acid while Fe^{2+} is a hard acid.

3. Alkyl free radicals,
(a) have unpaired electron on the carbon atom.
(b) are paramagnetic.
(c) are formed by heterolytic cleavages.
(d) have long-life than aryl free radicals.

4. Pick up the incorrect statements.
(a) Carbocation can act as electrophile and carbanion can act as nucleophile.
(b) Carbocation is pyramidal and carbanion is planar structure.
(c) In carbocation, the carbon bearing positive charge is sp^3 hybridised.
(d) Primary carbanion is more stable than secondary and tertiary carbanion.

5. With respect to carbenes, the true statements are:
(a) Carbon atom of a triplet carbene is sp hybridised and almost linear species.
(b) Carbon atom of a singlet carbene is sp^2 hybridised and angular species.
(c) The singlet carbene is more stable than the triplet carbene.
(d) Addition of singlet carbene to alkene is not stereospecific, while addition of triplet carbene to alkene is stereospecific.

6. When we compare the triple bonds present in benzyne and alkyne,
(a) the triple bonds are formed in both benzyne and alkyne by similar mechanism.
(b) in alkyne, π-bonds are formed by the overlap of $p_y - p_y$ and $p_z - p_z$ orbitals.
(c) in benzyne the π-bonds are formed by the overlap of $p_y - p_y$ and $p_z - p_z$ orbitals.
(d) in benzyne, the two π-bonds are formed by the overlap of $p_z - p_z$ and $sp^2 - sp^2$ orbitals.

7. Choose the correct statements.
(a) In chlorobenzene Cl activates the benzene ring by inductive effect.
(b) Cl activates the benzene ring by mesomeric effect.
(c) Cl deactivates the benzene ring by inductive effect.
(d) Cl deactivates the benzene ring by mesomeric effect.

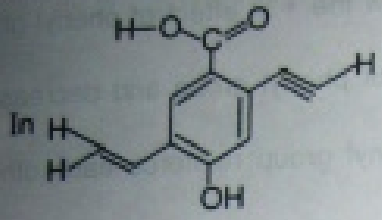
8. $C_6H_5CH_2COOH$ is stronger acid than acetic acid but C_6H_5COOH is weaker acid than formic acid. This is because
   (a) in phenyl acetic acid, phenyl group has an overall – I effect
   (b) in phenyl acetic acid, $-CH_2-$ group does not allow the + R effect of phenyl group to affect the acidic nature of – COOH group
   (c) in benzoic acid, + R effect overcomes – I effect of phenyl group and decreases the ionisation of – COOH group
   (d) in benzoic acid, + R effect and + I effect of phenyl group reinforce each other and decrease the ionisation of – COOH group

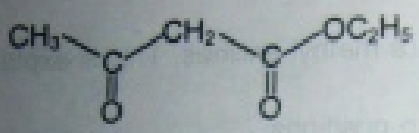
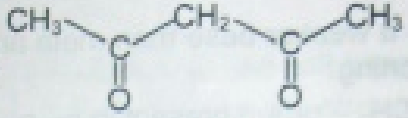
. o-methyl aniline is a weaker base than meta and para methyl anilines. This is explained by the following reasoning.
   (a) + I effect of $-CH_3-$ group present in o-, m- and p-positions
   (b) Conjugative effect of $-CH_3-$ group attached to the benzene ring
   (c) + I effect and conjugative effects of methyl groups attached to benzene ring
   (d) The stability of conjugate acid is less because of steric repulsion experienced by the added proton and the existing $-CH_3$ group at o-position

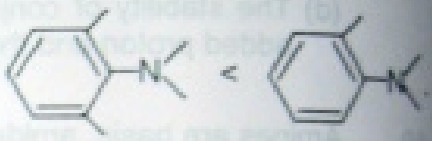
0. Amines are basic, amides are neutral and imides are acidic. These natures are due to
   (a) the alkyl groups attached to $-NH_2$ group exert + I effect; the N – H bond in imides is weakened by the adjacent C = O groups and + I effect of $R-C(=O)-$ group in amides makes less electron availability for donation
   (b) the alkyl groups attached to $-NH_2$ group exert + I effect; N – H bond in imide is strengthened by the adjacent $-\overset{\overset{O}{\|}}{C}-$ groups and + R effect of $R-\overset{\overset{O}{\|}}{C}-$ group in amides makes less electron availability for donation
   (c) the alkyl groups attached to $-NH_2$ group exert + I effect in amines, the N – H bond in imides is weakened by the adjacent $-\overset{\overset{O}{\|}}{C}-$ group and – I and – R effects of RCO – group in amides make less electron availability for donation.
   (d) the alkyl groups attached to $-NH_2$ group in amines exert + I effect; N – H bond in imides is strengthened by the adjacent carbonyl groups and + I and + R effect of RCO group in amides make less electron availability for donation

EXERCISE – III

SUBJECTIVE PROBLEMS

1. 
In , which hydrogen is the most acidic? Explain your choice.

2. 
(I)
and

(II)
When (I) and (II) are treated with base, separately carbanion results. Which carbanion will be more stable?

3. The basicity order of the following compounds is 
Explain the order.

4. Why do electrophiles attack trichloromethyl benzene at meta position whereas they attack benzene ring at ortho and para position in chloromethyl benzene?

5. $CH_3Cl + AgCN \longrightarrow$ Major product + Minor product. Describe the major product with reasoning.

6. $CH_2=CH-Cl$ does not give $CH_2=CH-OH$ easily on treatment with OH^-. Explain.

7. $CH{\equiv}CH \xrightarrow{HCl} CH_2=CH-Cl$

$CH_2=CH-Cl \xrightarrow{HCl} CH_3-CHCl_2$ (Possibility–1)

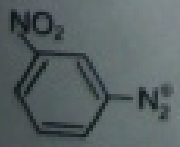
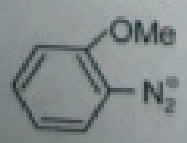
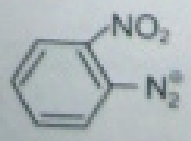
$CH_2=CH-Cl \xrightarrow{HCl} Cl-CH_2-CH_2-Cl$ (Possibility–2)

In the above reaction sequence if carbocation formation is the intermediate step, then out of the two possibilities, which one will be favoured?

8. Between, $\overset{|}{C}=\overset{|}{C}-\ddot{F}$ and $\overset{|}{C}=\overset{|}{C}-\ddot{Cl}$, which lone pair–$\pi$ conjugation will be more preferred?

9. Write the basicity order of NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ in aqueous medium.

10. Arrange the following electrophiles in the decreasing order of electrophilicity?


(I)

(II)

(III)

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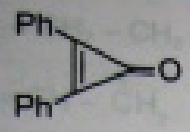
11. Give proper explanation/s for the following.

(a) Compound I has greater dipole moment than compound II.

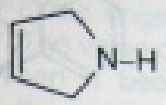


I

II

(b) Which compound has the greater electron density on its nitrogen atom?

or



(c) Species I is more stable than II.

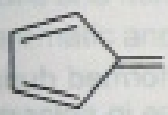
I

II

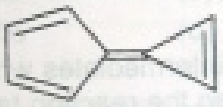
12. Give proper explanation/s for the following.

(a) A methyl group bonded to benzene loses proton more readily than a methyl group bonded to cyclohexane.

(b) The direction of the dipole moment in fulvene and calcene.

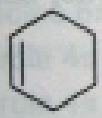


fulvene

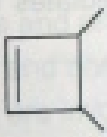


calcene

(c) Compound I is more stable than the compound II.



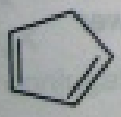
I



II

13. (a) If the pK_a of an acid is 6, what will be the pK_b of its conjugate base?

(b) Which of the following hydrocarbon is most acidic?

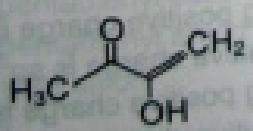
(i) 

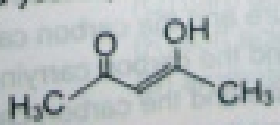
(ii)

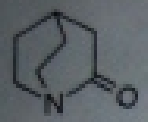
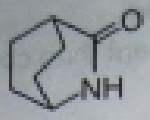
(iii)

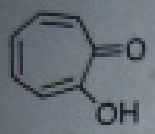
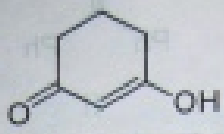
(iv)

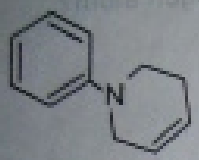
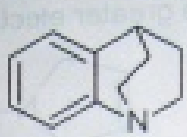
14. (a) Which of the two enols would you expect to be the stronger acid and why?



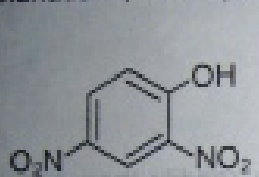
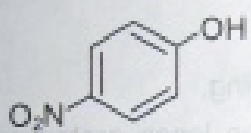
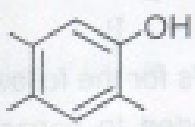
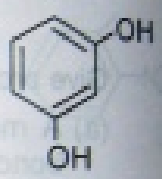


(b)  is basic but  is not.

(c)  is more acidic than 

(d)  is less basic than 

15. The phenols shown below have approximate pK_a values of 4, 7, 9, 10 and 11. Suggest with explanations, which pK_a value belongs to which phenol?

Comprehension I

The organic reactions proceed via some intermediates which are formed during the course of reaction and are not very stable species. When the reaction takes place in polar medium involving heterolytic cleavage, the intermediates are either carbonium ions or carbanions. If the reaction takes place at high temperature or in the present of u.v radiation, homolytic cleavage occurs and free radicals are formed as intermediates. Other intermediates like benzyne, carbene or nitrene are also formed in certain reactions.

1. Fe^{2+} ion is
   (a) a nucleophile and hard acid
   (b) an electrophile and a soft acid
   (c) a nucleophile and soft acid
   (d) an electrophile and a hard acid

2. H^+ ion is
   (a) a hard acid which is difficult to be oxidized and has higher polarizing power
   (b) is a soft acid which is easily oxidisable and has low polarizing power
   (c) is a nucleophile and a hard acid
   (d) is a nucleophile and a soft acid

3. True statement regarding the intermediate carbocation is
   (a) it has trigonal planar structure and the carbon carrying positive charge is sp^3 hybridised
   (b) it has pyramidal structure and the carbon carrying positive charge is sp^2 hybridised
   (c) it has trigonal planar structure and the carbon carrying positive charge is sp^2 hybridised
   (d) it has pyramidal structure and the carbon carrying positive charge is sp^3 hybridised

4. The unsaturated alcohol $CH_2 = CH - CH_2 - OH$ in acidic solution forms a carbocation. Its structure is

(a) $\overset{\oplus}{C}H_2 - CH_2 - CH_2 - OH$
(b) $CH_3 - \overset{\oplus}{C}H - CH_2 - OH$
(c) $CH_2 = CH - \overset{\oplus}{C}H_2$
(d) $CH_3 - CH_2 - \overset{\oplus}{C}H - OH$

Comprehension II

Organic compounds having planar cyclic rings containing $(4n + 2)\pi$ electrons involved in delocalisation possess aromic character. The value of n is a whole number. The above condition is called Huckel's rule of aromaticity. When n becomes a fractional value, the compound is non-aromatic. On the other hand when the number of electrons involved in delocalisation is 4n, then the compound is said to be anti-aromatic. Anti-aromatic compounds are less stable than aromatic or non-aromatic compounds.

1. But-1, 3-diene is
(a) a conjugated diene and aromatic
(b) a conjugated diene and non-aromatic
(c) a conjugated diene and anti-aromatic
(d) an isolated diene and non-aromatic

2. Cyclopropenium cation and cyclopentadienyl cation are respectively.
(a) Aromatic and non-aromatic
(b) Aromatic and anti-aromatic
(c) Non-aromatic and aromatic
(d) Anti-aromatic and aromatic

3. Both pyridine and pyrrole are aromatic yet pyrrole is less basic than pyridine. This is because
(a) pyridine has six membered while pyrrole has five membered ring structure
(b) in pyridine 6π electrons and one lone pair of electrons are involved in delocalisation
(c) in pyrrole 4π electrons and one lone pair of electrons are involved in delocalisation
(d) in pyrrole 4π electrons are involved in delocalisation

MATCH THE FOLLOWING

I.

(A) $R - NH_2$	(P) neither nucleophile nor electrophile
(B) $\overset{\oplus}{N}H_4$	(Q) anchimeric effect
(C) RMgX	(R) nucleophile
(D) σ-π conjugation	(S) nucleophile as well as electrophile

II.

(A) Tropylium cation	(P) anti-aromatic
(B) Cyclopentadienyl cation	(Q) hard acid
(C) Cyclopentadienyl anion	(R) soft acid
(D) Tropylium anion	(S) aromatic
(E) $H^{\oplus}$ ion	
(F) Ag^{+} ion	

ANSWERS TO EXERCISE – I

OBJECTIVE PROBLEMS WITH ONLY ONE CHOICE CORRECT

1. (c)	2. (a)	3. (d)	4. (c)	5. (a)
6. (b)	7. (d)	8. (a)	9. (a)	10. (b)
11. (b)	12. (a)	13. (b)	14. (a)	15. (d)
16. (a)	17. (b)	18. (a)	19. (d)	20. (d)

ANSWERS TO EXERCISE – II

OBJECTIVE PROBLEMS WITH ONE OR MORE THAN ONE CHOICE CORRECT

1. (a), (c)	2. (a), (b), (c)	3. (a), (b)	4. (b), (c)	5. (a), (b)
6. (b), (d)	7. (b), (c)	8. (a), (b), (c)	9. (d)	10. (c)

ANSWERS TO EXERCISE – III

SUBJECTIVE PROBLEMS

1. –COOH always shows stronger acidity as compared to other functional groups (except SO_3H).
2. Carbanion from (II) will be formed because of more thermodynamic stability due to greater resonance (as –COR group is more electron withdrawing than $-CO_2R$ group).
3. The basicity in the present case is influenced by solvation effect more than the availability of electron pair on nitrogen atom.
4. Participation of chlorine atoms in –H (Hyperconjugation).
5. CH_3NC. This is because of hard acid-hard base interaction (nitrogen atom is a harder acid than carbon).

6. This is because of lone pair–pπ conjugation in $CH_2=CH-Cl$ increases the bond order between C–Cl bond. Thus, C–Cl bond is not broken easily under milder conditions.

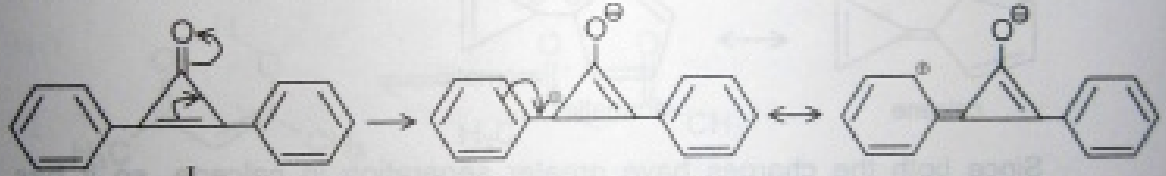
7. Possibility 1 will exist because $CH_2=CH-Cl$ on taking H^+ from HCl form $CH_3-\overset{\oplus}{C}H-Cl$, while in possibility II the carbocation formed is $\overset{\oplus}{C}H_2-CH_2-Cl$. The carbocation $CH_3-\overset{\oplus}{C}H-Cl$ is more stable than $\overset{\oplus}{C}H_2-CH_2-Cl$ because the former has +I effect of CH_3, +R effect of Cl and –I effect of Cl whereas the latter has –I effect of CH_2Cl. Thus, $CH_3-\overset{\oplus}{C}H-Cl$ is attacked latter by Cl^- to form CH_3CHCl_2 as the major product.

8. Lone pair–π conjugation between fluorine and carbon will be more effective than between chlorine and carbon (as Cl and C belong to 3rd and 2nd period respectively and F and C, both belong to 2nd period).

9. $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

10. (III) is the strongest electrophile because of –R effect of nitro group is also operative along with its –I effect but (I) has a greater +R effect (lesser –I effect) and NO_2 from meta position will only show –I effect. Thus, the decreasing order of electrophilicity is (III) > (I) > (II).

11. (a)



I

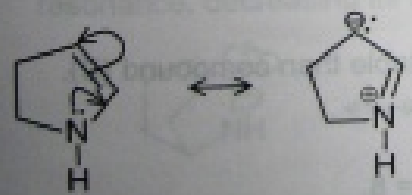
Highly strained ring

The +ve charge is resonance stabilized

II

Greater charge separation in I assigns it a higher dipole moment than II.

(b)

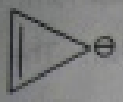


In N–H ; no such resonance is possible. Hence, electron density is more over nitrogen atom.

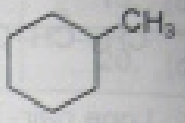
(c) is aromatic as it involves cyclic delocalization and follows Huckel's

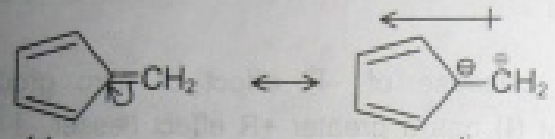
(I)

$(4n + 2)$ π-electron rule.

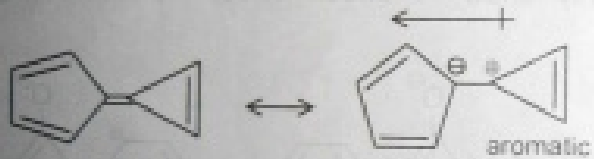
 is not aromatic and hence is less stable.

(II)

12. (a) In , the C–H bond is more polar than the C–H bond in  due to electron shift by hyperconjugative effect. Moreover, the loss of H^+ gives benzyl carbanion $Ph-\overset{\ominus}{C}H_2$, which is resonance stabilized but not so in the anion of methyl cyclohexane.

(b) 

fulvene aromatic

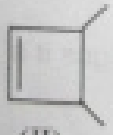


calcene aromatic

Since both the charges have greater separation in calcene, so it has more dipole moment than fulvene.

(c) . The sp^2 hybridised carbon is in a six-membered ring where the angle strain will

(I)

be less as compared to that in  where there is a four-membered ring, which is

(II)

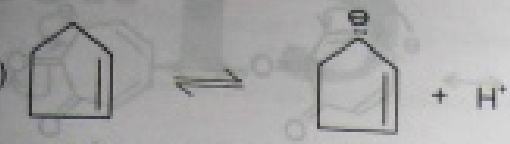
more strained. Thus, compound (I) is more stable than compound (II).

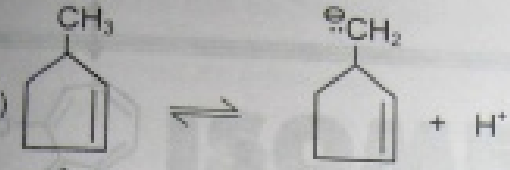
13. (a) $pK_a = 6$, pK_b of its conjugate base $= 14 - 6 = 8$.

(b) Cyclopentadiene is most acidic as the loss of proton in it gives a carbanion, which is stabilized by aromaticity.

(i) $+ H^+$

Most stable (aromatic)

(ii)  + H^+

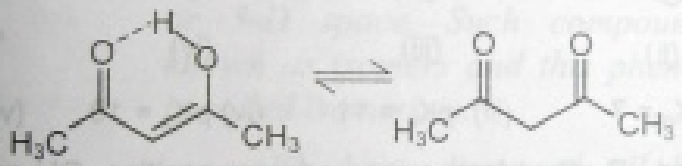
(iii)  + H^+

(iv) + H^+

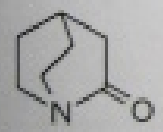
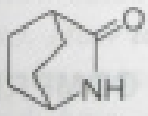
In case (i), the equilibrium is shifted most in the forward direction, hence compound (i) is most acidic.

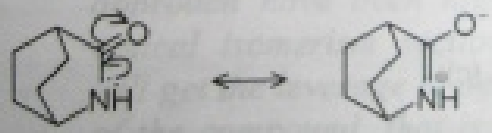
14. (a)

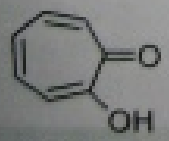
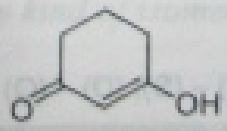
Both and –OH groups are in trans position and so no hydrogen bonding exists and can easily tautomerise and it is more polar.

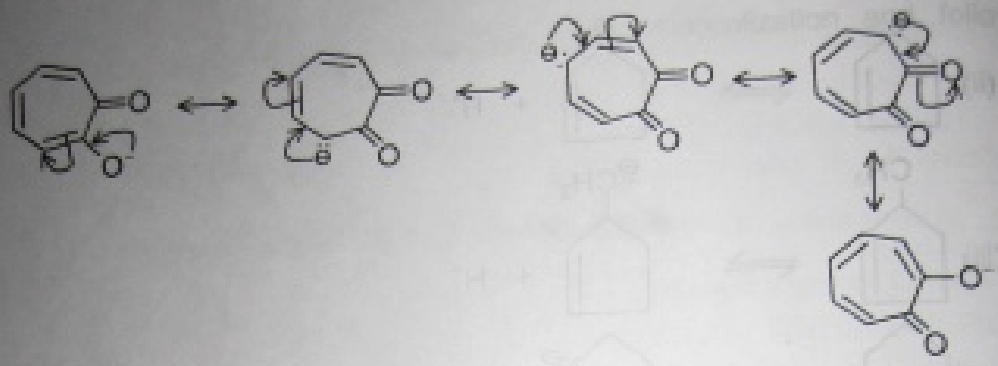


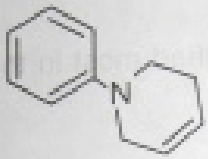
Here, intramolecular hydrogen bonding exists and is less polar. This compound is more acidic than the former as its carbanion is more resonance stabilized.

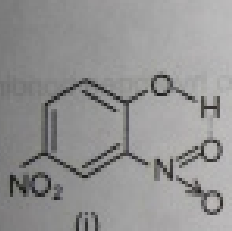
(b)  is basic but  is not because in the first case, the lone pair on nitrogen do not participate in resonance with $>C=O$ since it will generate a double bond on bridgehead position while in the second case it does participate in resonance, decreasing its basicity.

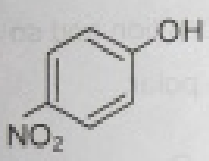


(c)  is more acidic than  because its conjugate base is more resonance stabilized.



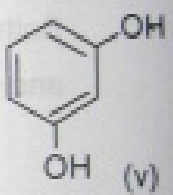
(d) The lone pair on nitrogen of  participates in resonance with phenyl ring, so it becomes less basic. This does not happens in

15. 
(i)


(ii)

(iii)

(iv)


(v)

(i) $pK_a = 4$ (ii) $pK_a = 7$ (iii) $pK_a = 11$ (iv) $pK_a = 10$ (v) $pK_a = 9$

NO_2 groups exerts –I and –R effect from ortho and para position. OH group exerts only –I effect from meta position. Me group exerts +I and +H effect from ortho and para position while it exerts only +I effect from meta position.

ANSWERS TO COMPREHENSIONS

Comprehension I

1. (b) **2.** (a) **3.** (c) **4.** (c)

Comprehension II

1. (b) **2.** (b) **3.** (c)

Match the following

I. (A) – (R); (B) – (P); (C) – (S); (D) – (Q)

II. (A) – (S); (B) – (P); (C) – (S); (D) – (P); (E) – (Q); (F) – (R)